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THERMAL DEGRADATION OF HIGH TEMPERATURE POLYMERS AND COMPOSITES

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13. ABSTRACT

A study was performed to examine the thermal degradation process and char forming characteristics of a number of polyquinoxaline polymers. The techniques employed consisted primarily of thermogravimetry, differential thermal analysis, and mass spectrometry. Constant heating rate and isothermal degradation experiments were carried out in vacuum, and to some extent, in air; the isothermal degradation rates were used to obtain an approximate activation energy for the degradation process.

The quinoxaline-based polymers showed improved thermal stability and greater carbon yields compared to conventional polymers. Thermal degradation occurred in three discrete steps, each accompanied by the evolution of characteristic volatile products. A phenyl-substituted polyquinoxaline degrades initially with evolution of benzene, toluene, and benzonitrile in the temperature range 525 to 600 C. The second step in the degradation, at 650 to 850 C, is accompanied by production of HCN and H_2. The final step occurs at 850 to 1400 C and is characterized by evolution of N_2. The behavior of phenyl ether substituted and crosslinked polyquinoxalines is similar in many respects; however, carbon yields are reduced and the primary degradation produces phenol, cresol, and carbon monoxide in addition to the aromatic hydrocarbons. The primary degradation is an exothermic process. It consists of rupture of substituents from the quinoxaline ring and cleavage of the ring itself. The observed volatile products, with the exception of benzonitrile, are probably secondary products stabilized by abstraction of hydrogen from neighboring aromatic rings. Generalized degradation mechanisms that have been derived for these polymers from combined mass spectrometry and residue analysis results are described.

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THERMAL DEGRADATION OF HIGH-TEMPERATURE POLYMERS AND COMPOSITES

to

NAVAL ORDNANCE LABORATORY
WHITE OAK

June 23, 1972

Prepared Under Contract N 60921-71-C-0250

by

C. A. Gaulin
W. H. Pfeifer

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FOREWORD

This report was prepared by Battelle's Columbus Laboratories, 505 King Avenue, Columbus, Ohio, for the Naval Ordnance Laboratory, White Oak, Silver Springs, Maryland, under Contract N 60921-71-C-0250. The bulk of the technical work was performed by the Aerospace Corporation, 2300 East El Segundo Boulevard, El Segundo, California, under BCL subcontract D-5313. The project engineer for BCL was W. H. Pfeifer. The principal investigator for Aerospace was C. A. Gaulin.

This report covers work accomplished in the period 24 June 1971, to 29 May 1972.

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The authors wish to express appreciation for the invaluable assistance of D. E. Gilmartin and M. Buechler, the former for help and suggestions in carrying out the mass spectrometric study and the latter for his contributions to the thermal aspects of the study as well as suggestions for improvements in data handling and equipment design. W. T. Barry, Jr., contributed liaison and coordination for the program and participated in helpful discussions.

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ABSTRACT

Projected reentry vehicle requirements indicate that performance of future thermal protection systems will depend to a large extent on the availability of advanced ablative materials with increased hardness potential and of carbon/carbon composite heat shields. In order to fulfill these objectives, it is necessary to provide materials with capabilities beyond those of the current phenolic polymer-based systems. A promising area of investigation lies in new high-temperature polymer technology.

This program has been devoted to studying the thermal degradation process and char forming characteristics of a number of polyquinoxaline polymers. The techniques employed have been primarily those of thermogravimetry, differential thermal analysis, and mass spectrometry. Constant heating rate and isothermal degradation experiments have been carried out primarily in vacuum and to some extent in air atmosphere. The isothermal degradation rates have been used to obtain an approximate activation energy for the degradation process.

The quinoxaline-based polymers have shown improved thermal stability and greater carbon yields than conventional polymers. Thermal degradation has been shown to occur in three discrete steps, each accompanied by the evolution of characteristic volatile products. A phenyl-substituted polyquinoxaline degrades initially with evolution of benzene, toluene, and benzonitrile in the temperature range 525 to 600°C. The second step in the degradation, at 650 to 850°C, is accompanied by production of HCN and H_2. The final step occurs at 850 to 1400°C and is characterized by evolution of N_2. The behavior of phenyl ether substituted and crosslinked polyquinoxalines is similar in many respects; however, carbon yields are reduced and the primary degradation produces phenol, cresol, and carbon monoxide in addition to the aromatic hydrocarbons. The primary degradation is an exothermic process. It consists of rupture of substituents from the quinoxaline ring and cleavage of the ring

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itself. The observed volatile products, with the exception of benzonitrile, are probably secondary products stabilized by abstraction of hydrogen from neighboring aromatic rings. Generalized degradation mechanisms that have been derived for these polymers from combined mass spectrometry and residue analysis results are described.

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I. INTRODUCTION

Recent trends in the development of reentry vehicles, both ballistic and maneuvering, have placed a two-fold emphasis on thermal protection development. The two approaches involve development of improved ablative materials with increased hardness potential and of carbon/carbon composite heat shields for advanced decoyable systems. Both approaches have a common requirement for forming a durable carbonaceous matrix, the former under the transient condition of reentry and the latter under the controlled conditions of fabrication. It is the char forming mechanism for both ablatives and carbon matrix precursors that will be emphasized in this study, along with the necessary kinetic data for use in analyt al models to predict ablation performance where ground simulation is not feasible.

Much of this work has been carried out on phenolic materials, and their limitations in both areas are reasonably well established. The principal area for developing improved materials lies in the high-temperature polymer technology currently being developed. The polyaromatic (polyphenylenes, polyacetylenes) and polyaromatic heterocyclic polymers in particular hold promise for superior ablation performance, improved high-temperature properties, and greater char yields. The materials of primary interest in this program are a number of polymers based on recurring units of quinoxaline (Refs. 1-8).

The objective of this program is to study the degradation process of new high-temperature and high char yield polymers in order (1) to obtain rates of decomposition for incorporation into analytical models for predicting performance and sizing of heat shields for typical reentry trajectories; and (2) to gain insight into mechanisms of char formation that will lead to improved charring ablators and to high yield carbon matrix precursors for application to new carbon/carbon and monolithic graphites. Microwave energy will also be evaluated as a potential method of achieving rapid decomposition in typical reentry materials.

II. PROCEDURE AND RESULTS

A. MATERIALS

Chief among the materials of interest to this program as high temperature heterocyclic polymers having innate high carbon yields is the class of resins based on recurring units of quinoxaline. Phenyl and phenylene oxide substituted quinoxalines are representative of this class of materials offering high resistance to long term thermal and oxidative environmental exposure. All of the materials studied in this program were supplied for this purpose by Whittaker Corporation*. For purposes of this report, a simple number has been assigned to each material for identification. These numbers are cross-referenced to the Whittaker codes and the corresponding polymer structures are given in Table 1. A detailed description of the monomer and polymer preparations is available in a Whittaker report (Ref. 9). All polymer specimens were supplied in the "cured" condition. In addition to the neat polymers, a composite sample was included in this study. The composite was fabricated from a phenylene oxide crosslinked polyquinoxaline (Polymer IV) with a carbon fiber (Modmor II) reinforcement. The sample was identified as being a representative section of Whittaker Panel No. 6 and contained a nominal 40 wt % of polymer.

B. DEGRADATION STUDIES

The polymers in this study were investigated primarily through the use of the techniques of thermogravimetry and mass thermal analysis. The latter method (Ref. 10) employs a special high-vacuum cell with a DuPont 900 thermoanalyzer to program linearly the temperature of a sample while a fraction of the volatile products is continuously pumped into the ion

*Research and Development Division, 3540 Aero Court, San Diego, California 92123

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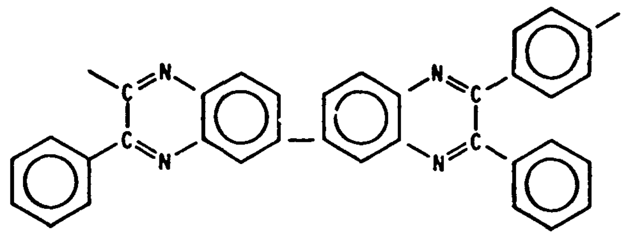
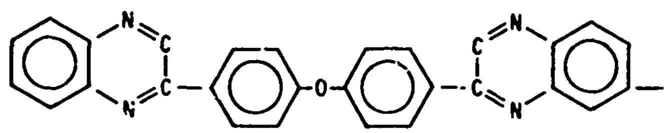
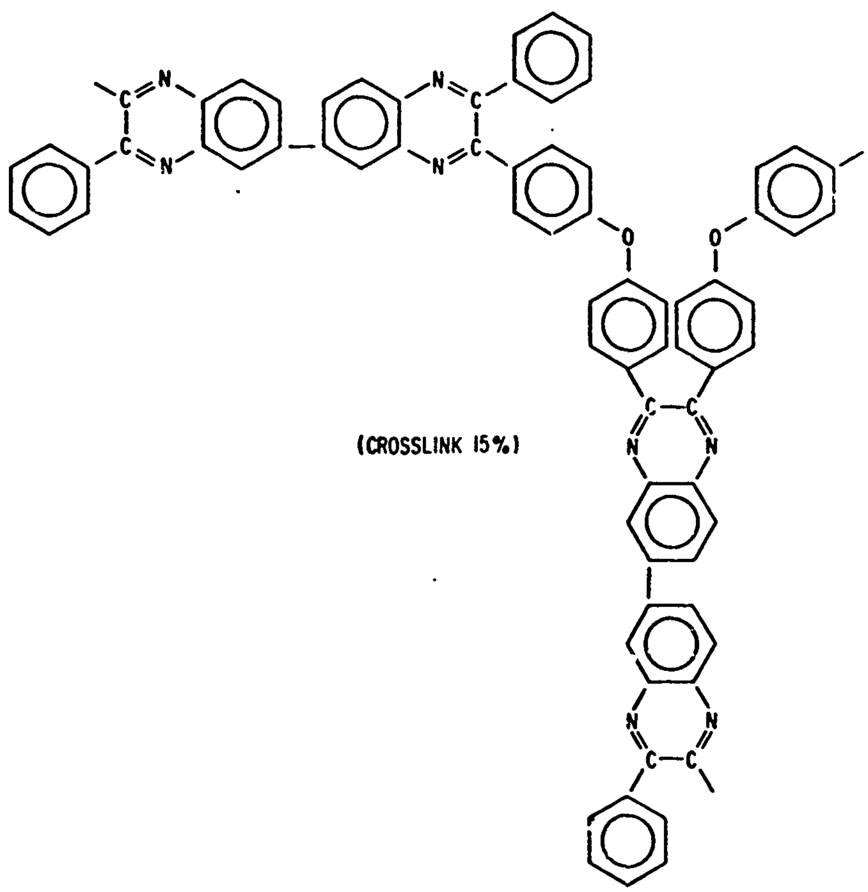
Table 1. Polymers Investigated in This Program

POLYMER No.	CODE	MONOMER UNIT STRUCTURE
I	PPQ-NAV-P-12	
II	PQ-RR-3106-14	
III	PPQ TRIFUNCTIONAL RR-272-32	 (CROSSLINK 15%)
IV	PPQ TRIFUNCTIONAL PGB/36% x - 361	SAME AS III ABOVE (CROSSLINK 36%)

source of a high resolution mass spectrometer (CEC-110-B) through a specially constructed beam-forming device. Four parameters are monitored continuously during an experiment: (1) the sample's thermal response, (2) the pressure of the evolved gases above the sample, (3) the mass spectrum of these gases, and (4) the sample temperature.

Vacuum thermogravimetry (TGA) was carried out on the polymers, in most cases to 1100°C. Pressure in the system was maintained in the 10^{-4} torr range, and a heating rate of 5°C/min was used. Figures 1 through 4 show the results of the vacuum TGA experiments for the individual polymers. The key features of the thermograms are summarized in Table 2. Briefly, Polymer I (Fig. 1), shows the onset of thermal degradation at approximately 525°C, with a steep drop in the weight curve occurring between 550 and 600°C. The latter region corresponds to the temperature range of most rapid decomposition. This is followed by a knee in the curve and a subsequent steep inflection in the range 725 to 775°C. The inflection is evidence of a secondary decomposition reaction. The curve then flattens to 920°C, and there is an indication of the onset of a third weight loss mechanism in the vicinity of 950°C. This latter mechanism persisted until 1100°C, until overall residue or char yield under these conditions amounted to 66.5%.

The behavior of the other polymers (Figs. 2, 3, and 4) is similar with the exception of the characteristics noted in Table 2. In addition, Polymers II and IV exhibit measurable weight loss in the initial portion of the heat treatment, at temperatures well below the onset of degradation. The weight losses amount to approximately 1 and 2 wt % for Polymers II and IV, respectively. These anomalies may be indicative of residual incompletely reacted ingredients, reflecting an inadequate cure cycle.

As observed in a TGA experiment, the composite specimen initially experiences a gradual 0.5 wt % loss prior to onset of degradation (Fig. 5). The inflection which signals the onset of thermal degradation is gentle and is consequently difficult to pinpoint precisely. It appears to be in the

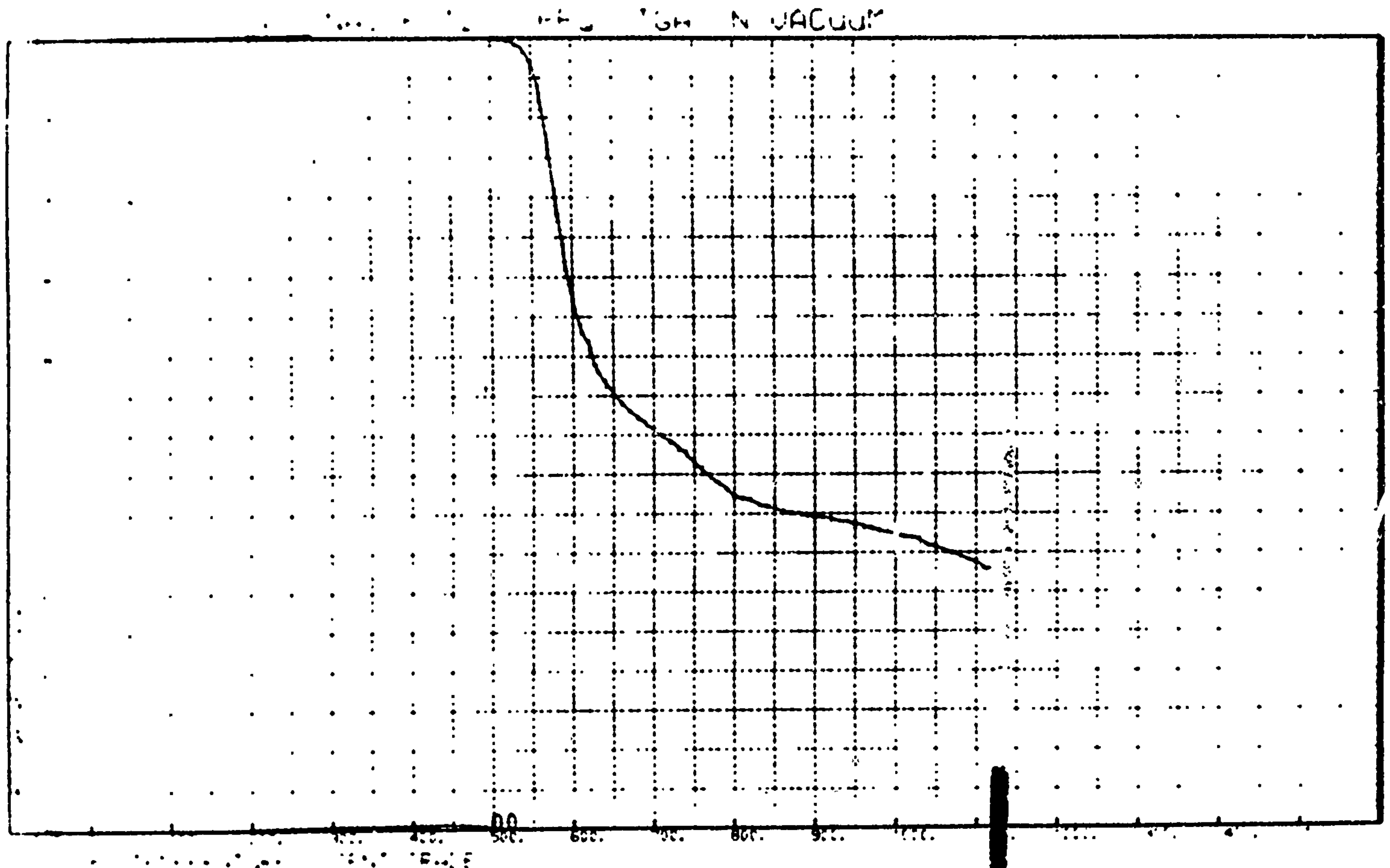


Fig. 1. Thermogravimetry in Vacuum of Polymer I

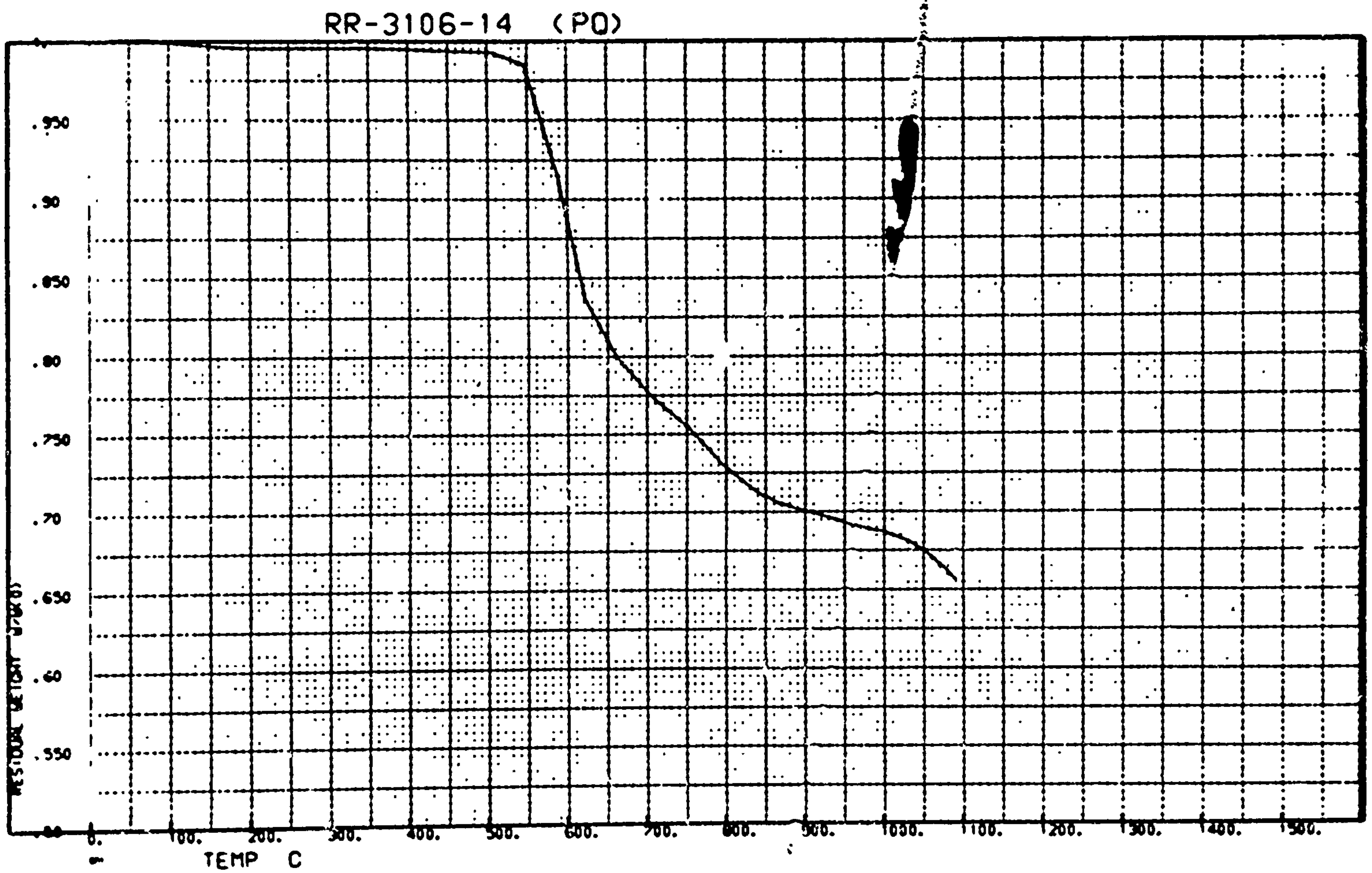


Fig. 2. Thermogravimetry in Vacuum of Polymer II

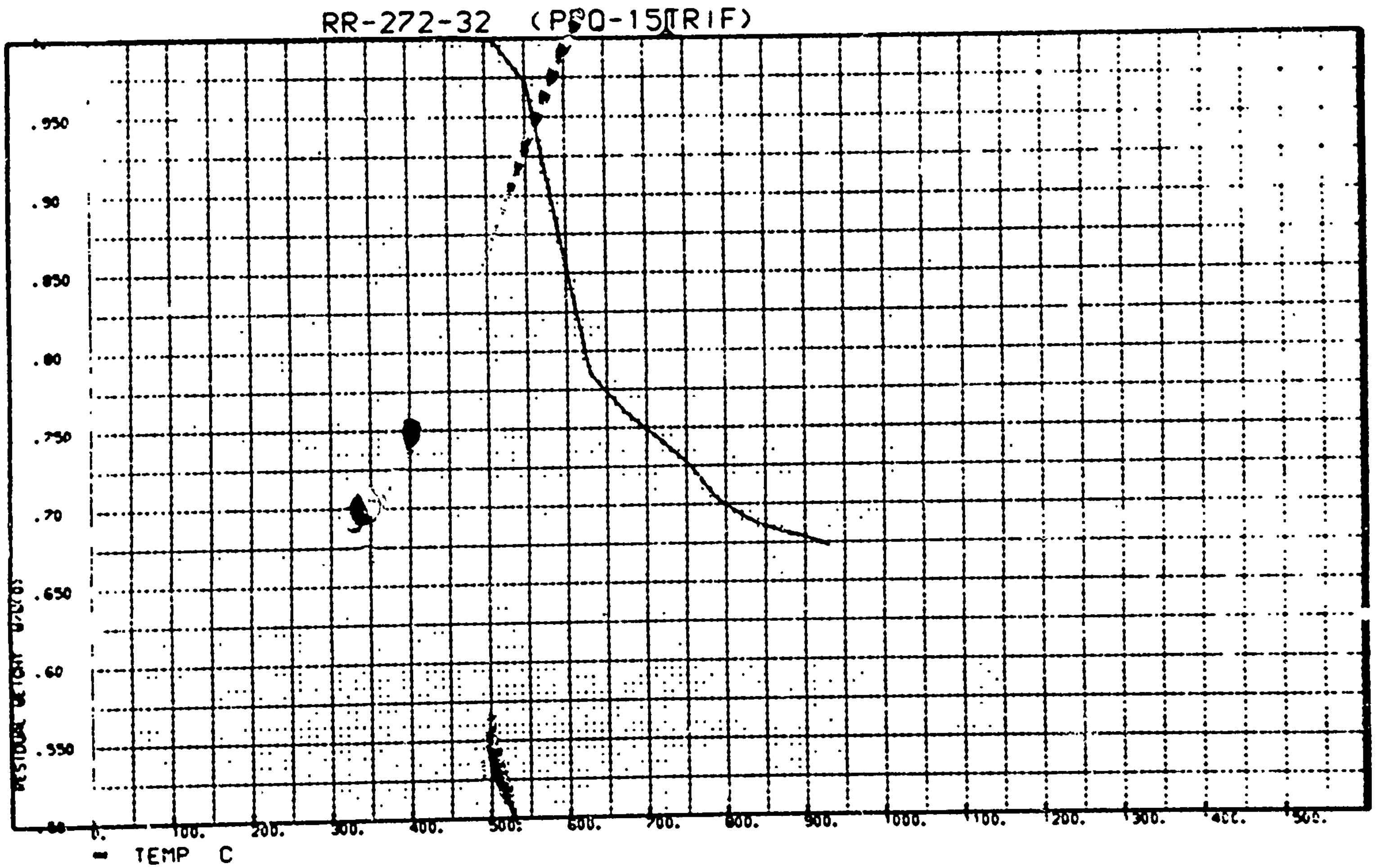


Fig. 3. Thermogravimetry in Vacuum of Polymer III

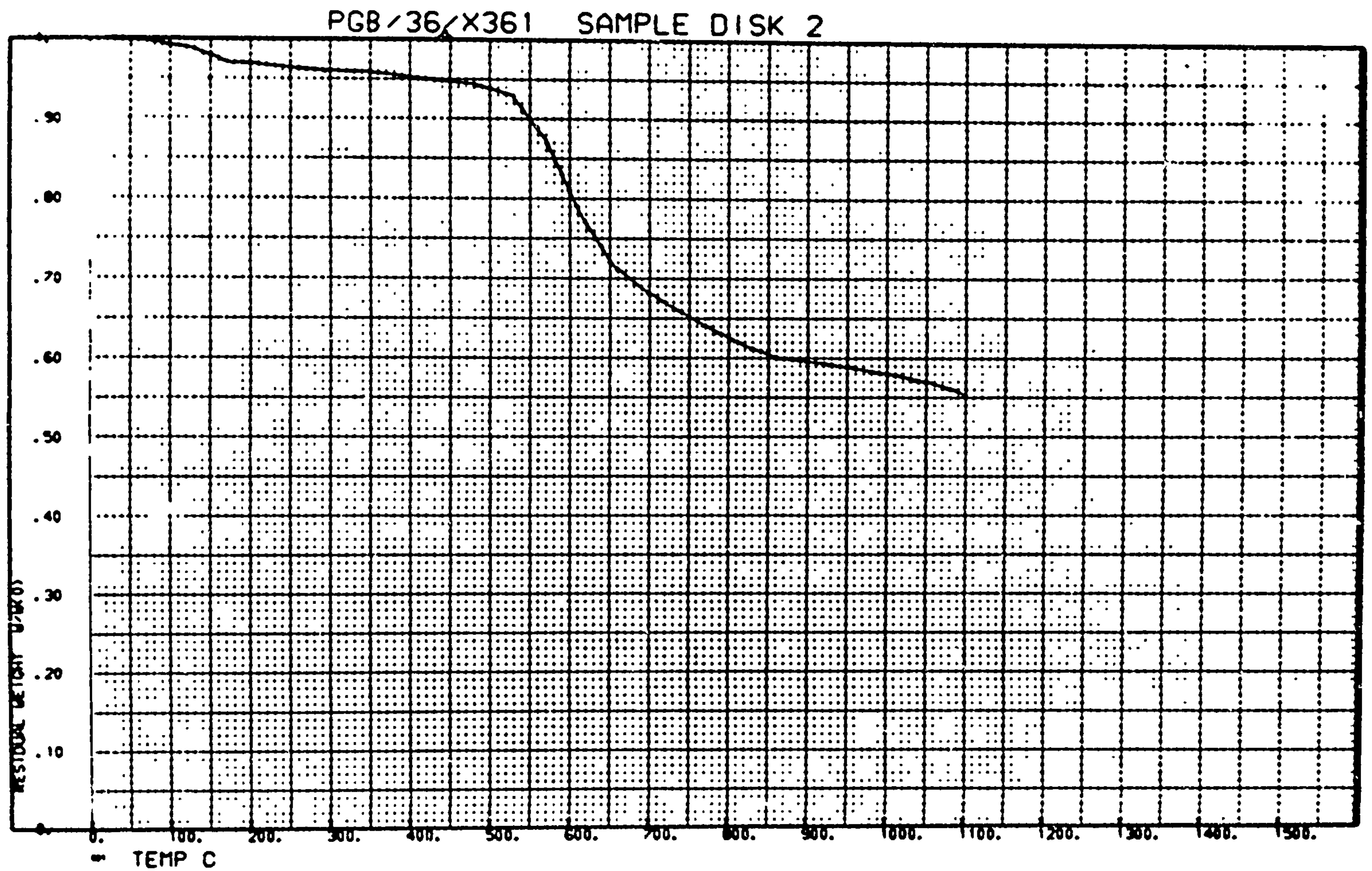


Fig. 4. Thermogravimetry in Vacuum of Polymer IV

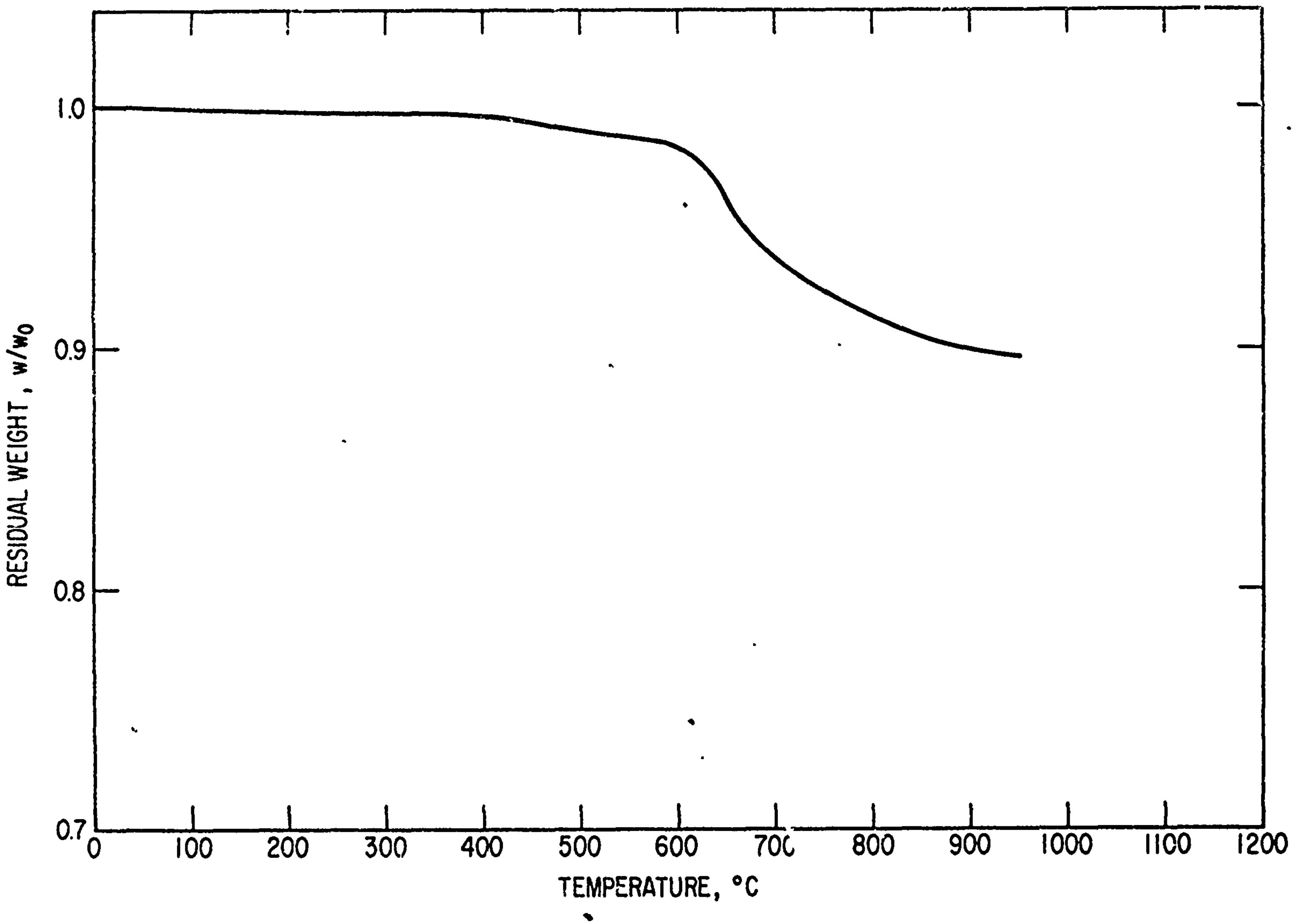


Fig. 5. Thermogravimetry in Vacuum of Composite

neighborhood of 450°C. Ultimate carbon yield (at 900°C) is 89 wt %, considerably higher than expected in simple proportion to the resin content. It is tempting to suggest a stabilizing effect due to the presence of the particular reinforcement. The significance of this result merits further investigation.

For purposes of better defining the temperature of maximum degradation rate, data from thermogravimetry have been treated, in two instances, to generate differential thermograms (DTG). The differential thermograms for vacuum degradation of Polymers I and IV are presented in Figs. 6 and 7, respectively. The principal peaks of these DTG curves each occur at 570°C, indicating no significant difference in T_{max} between the phenyl substituted linear Polymer I and the highly crosslinked Polymer IV.

The thermal oxidative stability of the polyquinoxaline was considered by carrying out a TGA experiment similar to the above but in air atmosphere. The result of such an experiment for Polymer I, degraded at a heating rate of 5°C/min in air at 1 atm, is reproduced in Fig. 8. The experiment reveals no susceptibility to oxidative attack below the expected degradation temperature (about 500°C). The primary degradation, T_{max}, is similar to that in vacuum; however, not surprisingly, the polymer is entirely consumed at 650°C.

The phenylene oxide crosslinked polymer (Polymer IV) was subjected to similar treatment. In this case, the onset of oxidative attack occurs at a somewhat reduced temperature (400°C). The remainder of the TGA curve (Fig. 9), however, indicates greatly enhanced resistance to oxidative degradation at extreme temperatures, such that the polymer is not completely oxidized until over 900°C is reached. This latter effect is even more pronounced in the case of the composite (Fig. 10), where the onset of degradation is detected at 500°C, followed by a very gradual oxidative degradation. At 600°C in air the residual weight is 90%, while even at 1130°C (the temperature limit of the apparatus), 25 wt % of the composite remained as residue. This must be considered remarkable high temperature oxi-

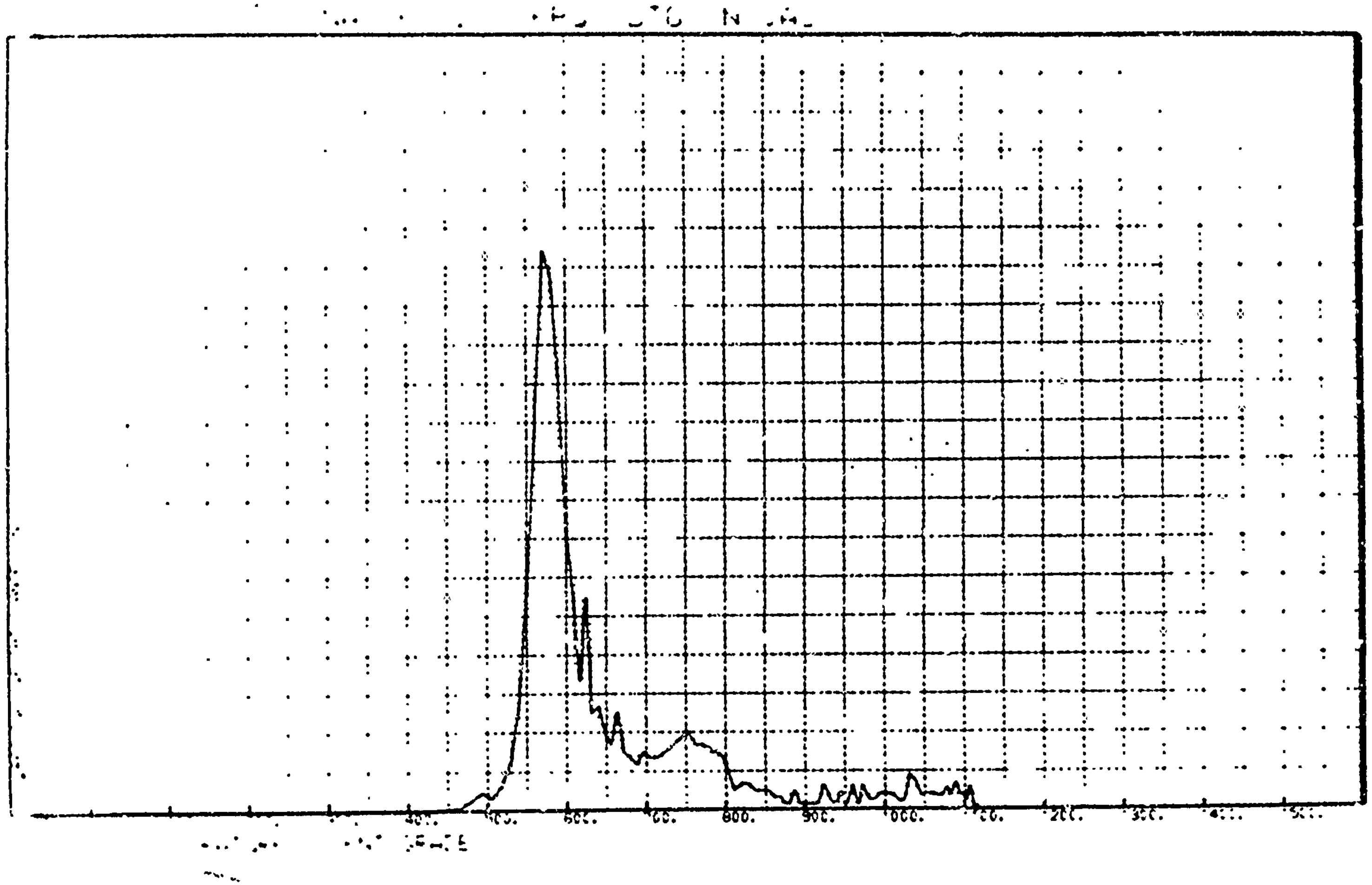


Fig. 6. Differential Thermogram of Polymer I in Vacuum

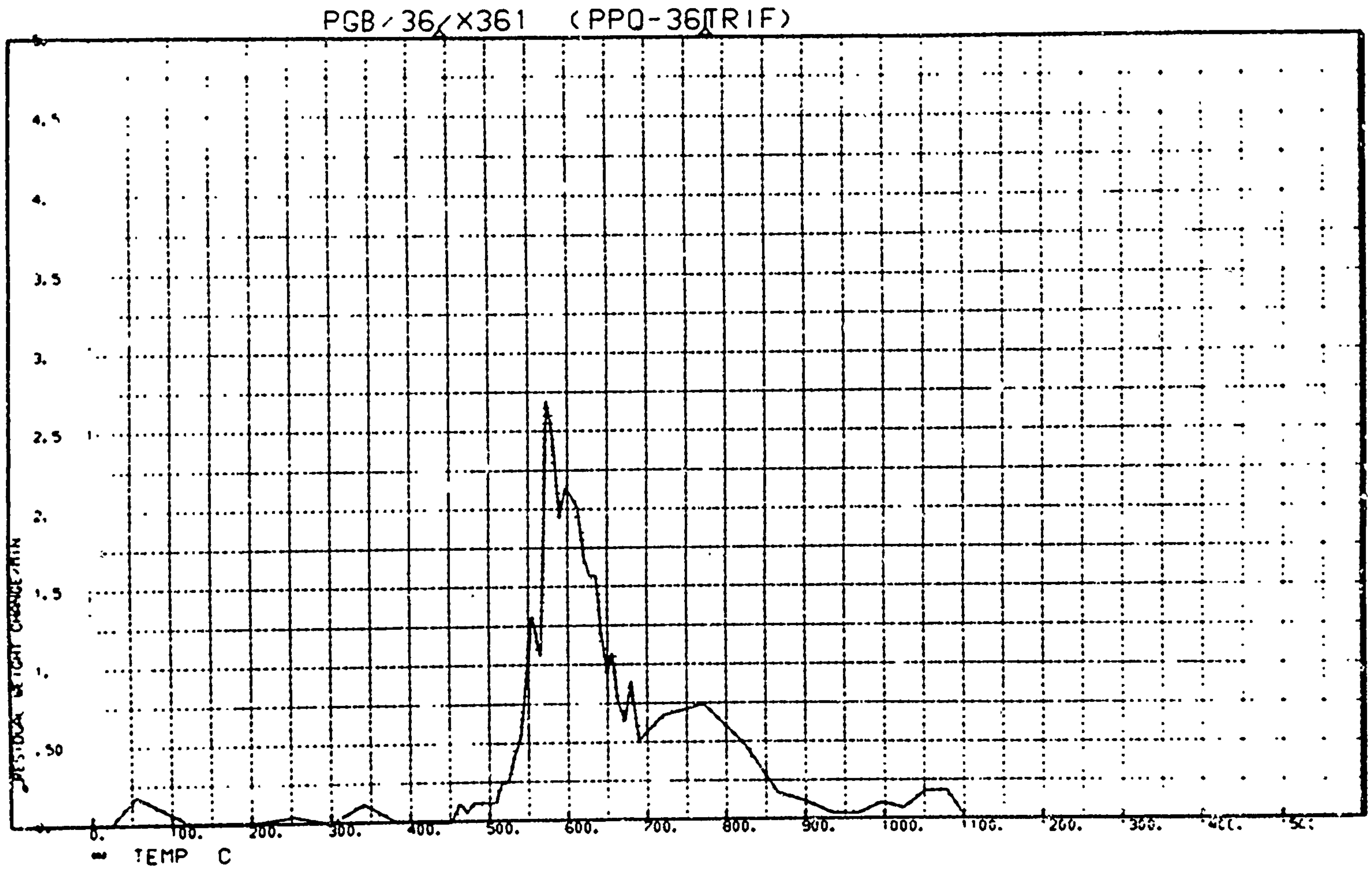


Fig. 7. Differential Thermogram of Polymer IV in Vacuum

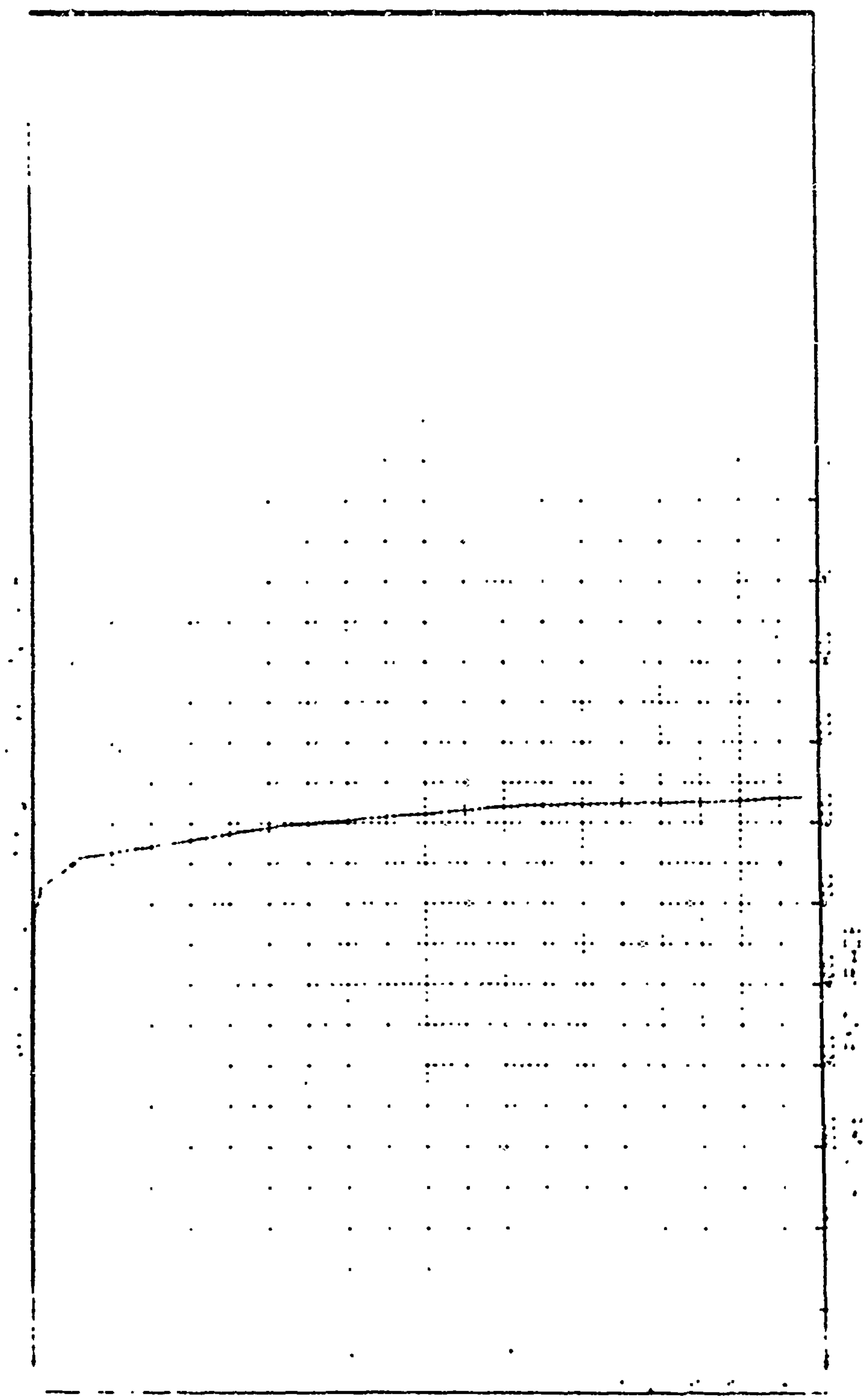


Fig. 8. Thermogravimetry in Air of Polymer I

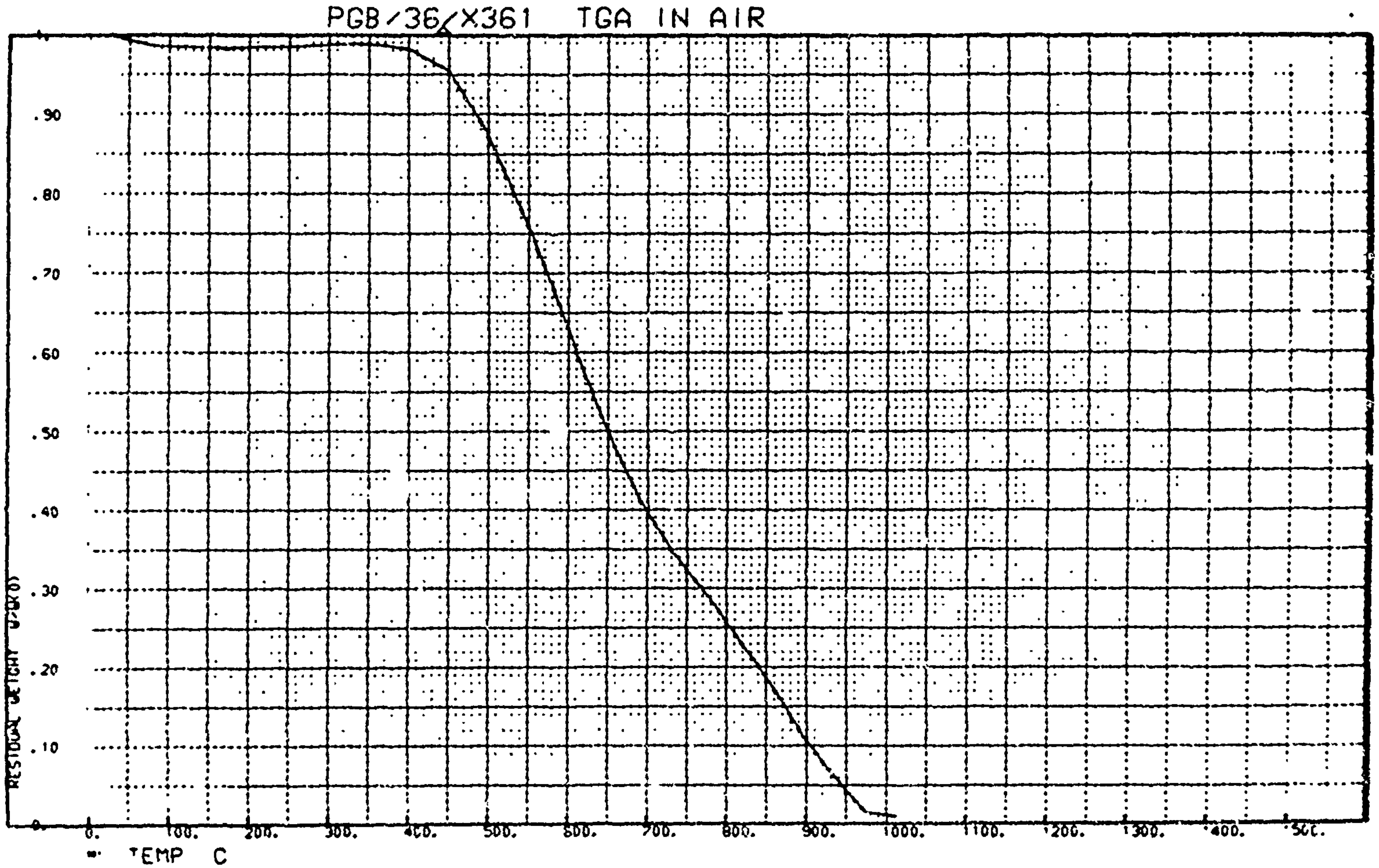


Fig. 9. Thermogravimetry in Air of Polymer IV

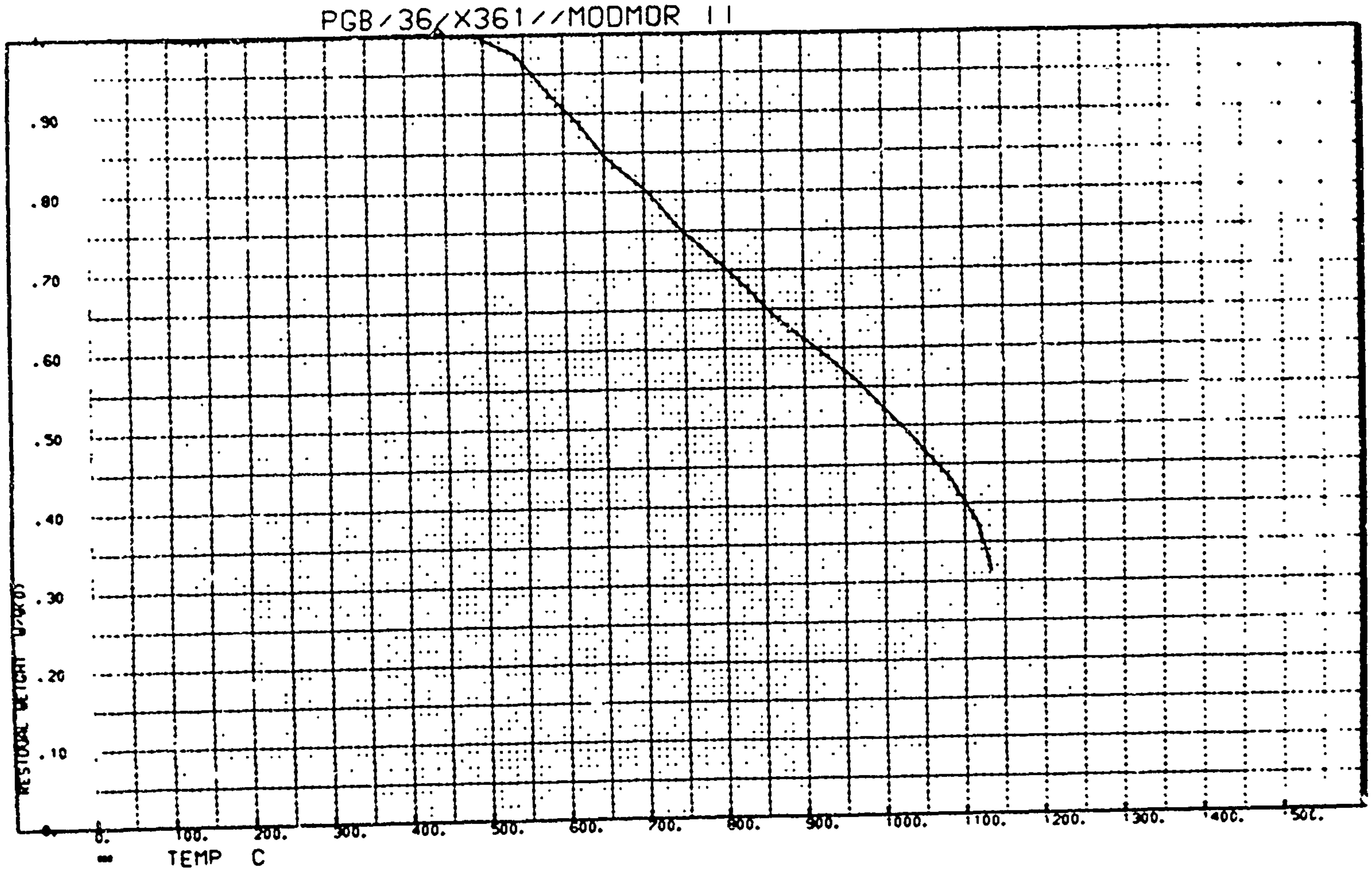


Fig. 10. Thermogravimetry in Air of Composite

Table 2. Summary of Thermal Characteristics of Polymers

Polymer No.	T_D, $^oC^a$	T_{max}, $^oC^b$	Carbon Yield, wt %[c]
I	525	570	66.5
II	515		65.5
III	515		64.5[d]
IV	480	570	54.5

a. Temperature for onset of decomposition, by TGA

b. Temperature for maximum rate of weight loss, by DTG

c. Ultimate residue, by programmed TGA, at 1100°C

d. Extrapolated from 900°C

dative stability for an organic system and has important implications with regard to long term elevated temperature exposure in air. This revelation merits further study.

Mass thermal analyses were carried out to 1450°C with a nominal heating rate of 10°C/min. The heating rate may vary slightly from the nominal and also deviate slightly from linearity; however, a typical rate curve is shown in Fig. 11, with temperature shown as a function of time. The initial sample cell pressure is usually on the order of 10^{-7} torr. In the normal operating mode, the mass spectrometer is set to scan magnetically through the entire temperature program to provide as broad a coverage as possible of the masses generated. In some instances, where it is desired to obtain more rapid recording of a narrower mass range, this is accomplished by continuous electrostatic scanning. Normal instrument conditions are a 50 eV ionization potential and a set resolution of 1:2500 amu.

Mass thermal analysis provides a record of the differential thermal response of a specimen simultaneously with mass spectrometric analysis of volatile degradation products. In order to establish the polarity of the DTA,

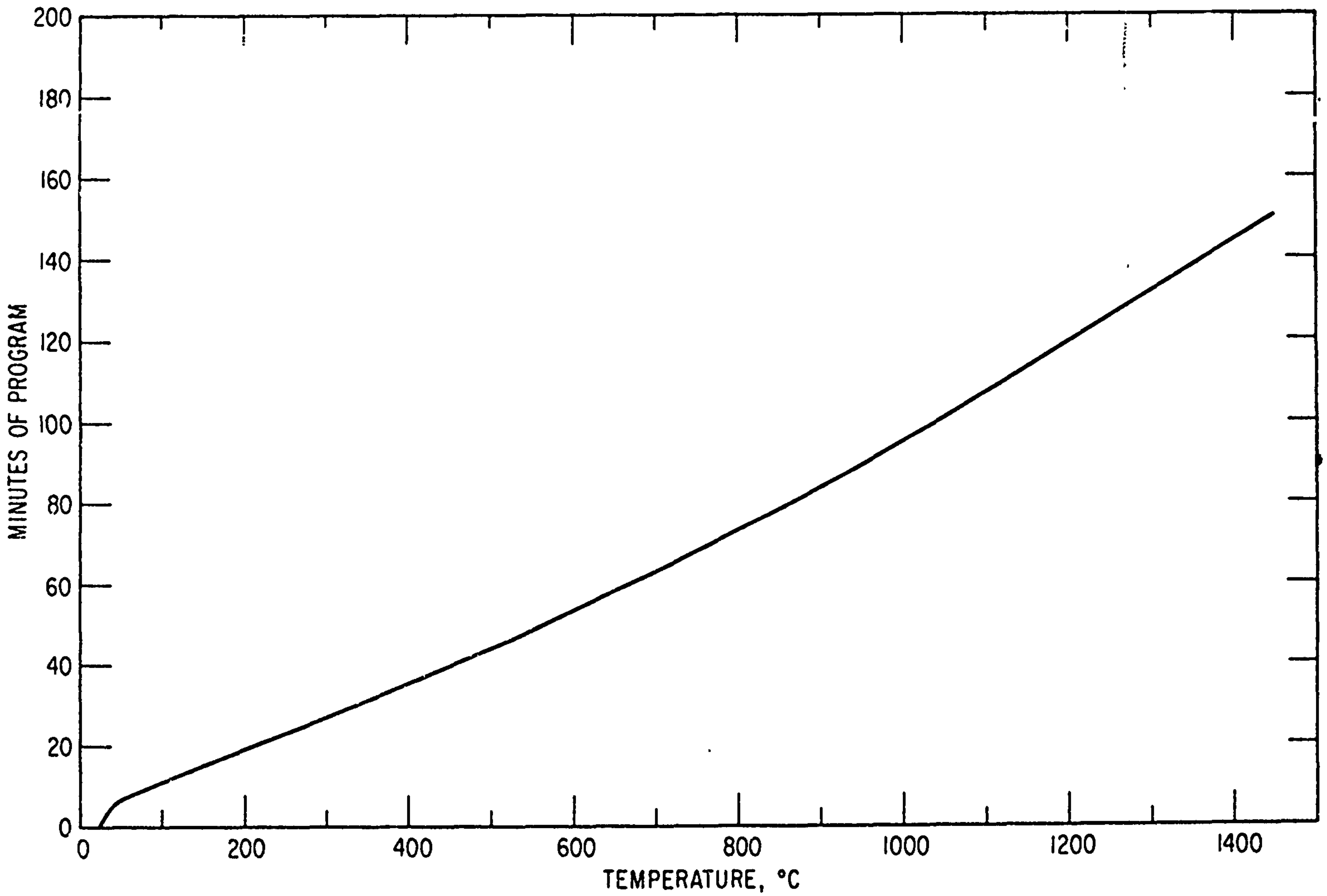


Fig. 11. Typical Heating Rate Curve for Mass Thermal Analysis

it is customary occasionally to record the differential trace of a known material for use as a calibration source. In this laboratory, the practice has been to employ silica as the calibration standard. A typical DTA calibration curve as recorded on this apparatus is presented in Fig. 12. The expected endothermic transition from α to β quartz is observed at 570°C.

Each of the vacuum DTA records obtained for the polyquinoxaline polymers show marked exotherms. The peak temperature of the individual exotherms varies between 550 and 575°C, as shown in Figs. 13 through 16. No particular emphasis should be given to these small differences, since the DTA curves of polymers in general are characteristically broad and are subject to some variability in peak response temperature due simply to small differences in compactness of packing in the cell, sample settling, or separation accompanying degradation. Generally, the observed exotherms are in excellent agreement with the maximum weight loss temperatures as seen by TGA. With respect to DTA, no additional thermal responses were detected for any of the polymers up to 1450°C. The thermogram obtained for the composite specimen is presented in Fig. 17. The exothermic response observed is identical in every respect with those of the non-reinforced polymers.

DTA of Polymer I also was investigated in air atmosphere. As seen in Fig. 18, the method is very sensitive under these conditions. The curve shows the onset of an exothermic response in the vicinity of 420°C, followed by a gradual increase in slope up to a peak at 581°C, when sudden and severe oxidation occurs, resulting in complete loss of residue at 600°C. This result is in excellent agreement with the TGA curve of Fig. 8.

Mass thermal analysis lends itself readily to monitoring the pressure of the gases and vapors generated during the degradation of a polymer. In a typical experiment, the pressure is monitored continuously in two locations: in the ion source of the mass spectrometer and at the differential pumping station used to maintain vacuum in the DTA cell. The pumping station is a high-speed Veeco oil diffusion pumped system. It is particularly instructive to record continuously the pressure at this point as a function of sample

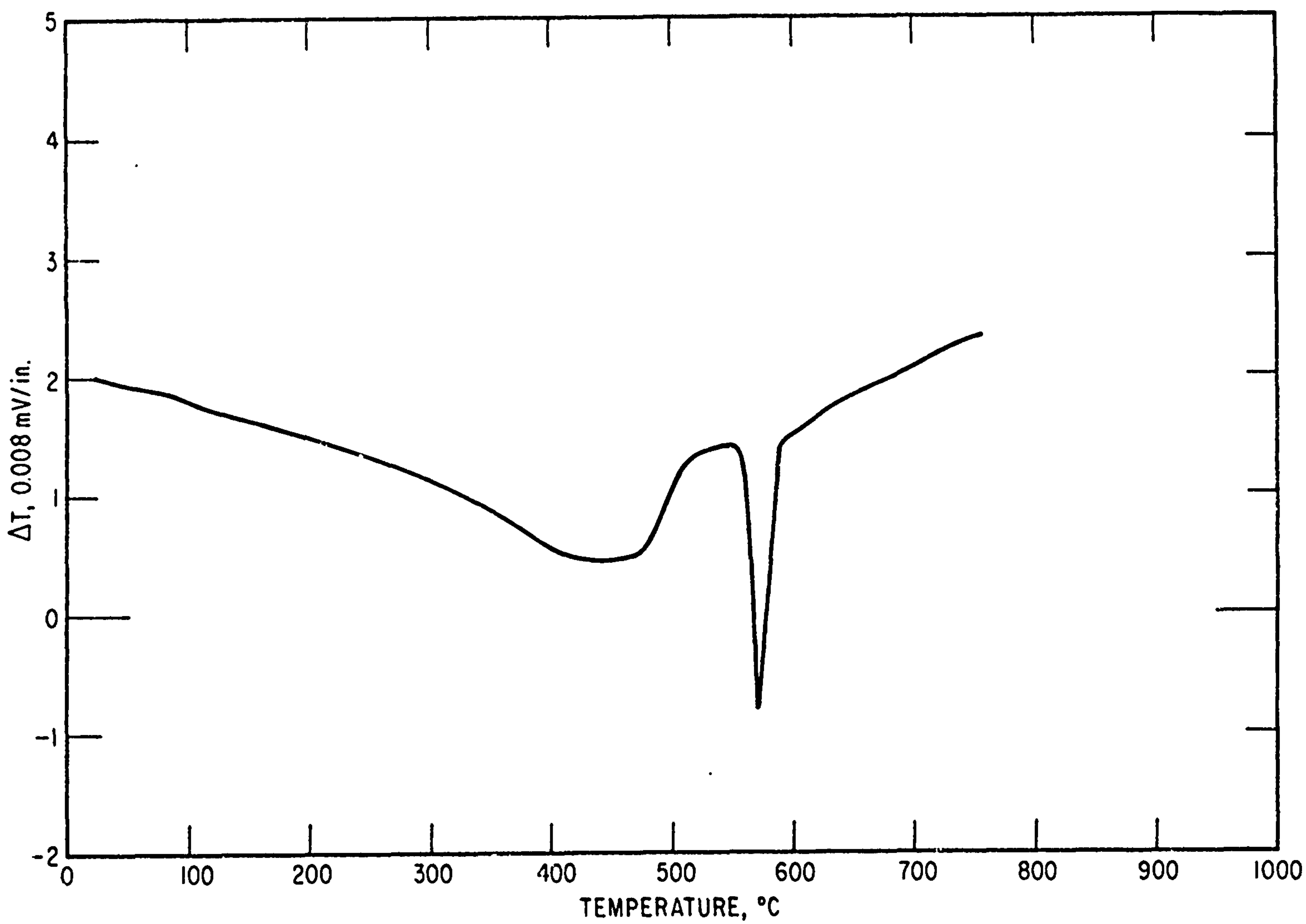


Fig. 12. DTA Calibration Curve for Silica

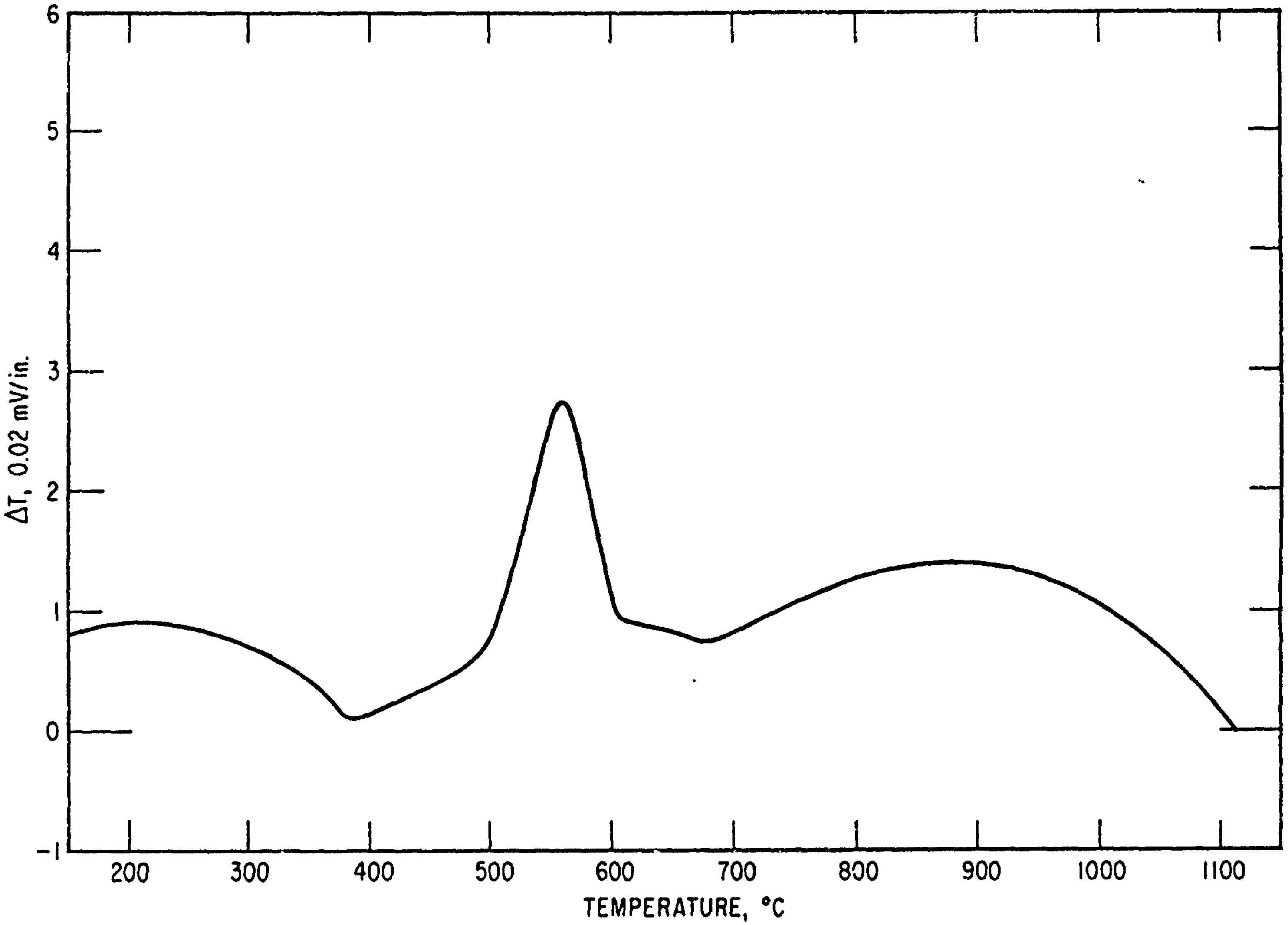


Fig. 13. DTA Curve in Vacuum for Polymer I

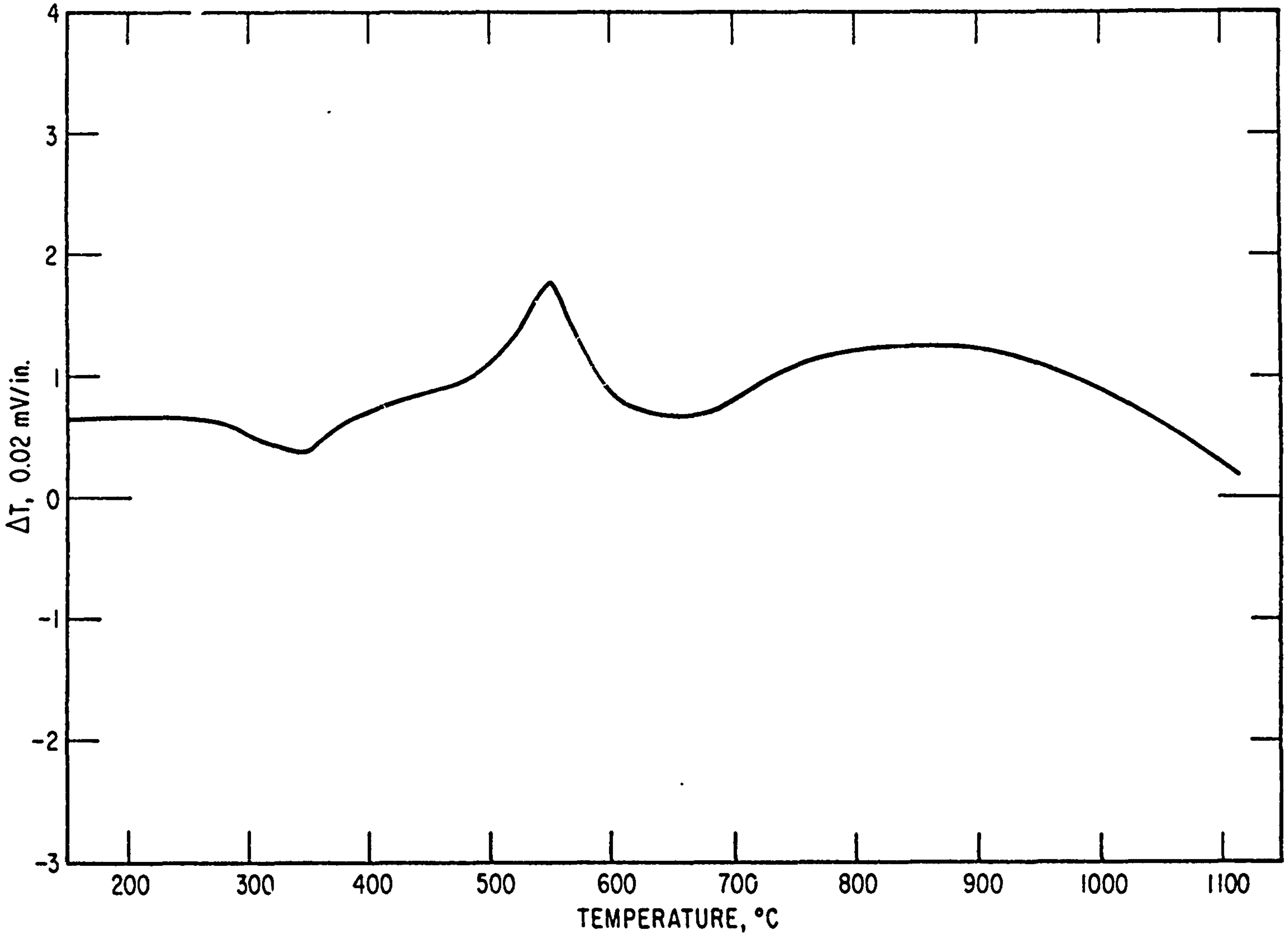


Fig. 14. DTA Curve in Vacuum for Polymer II

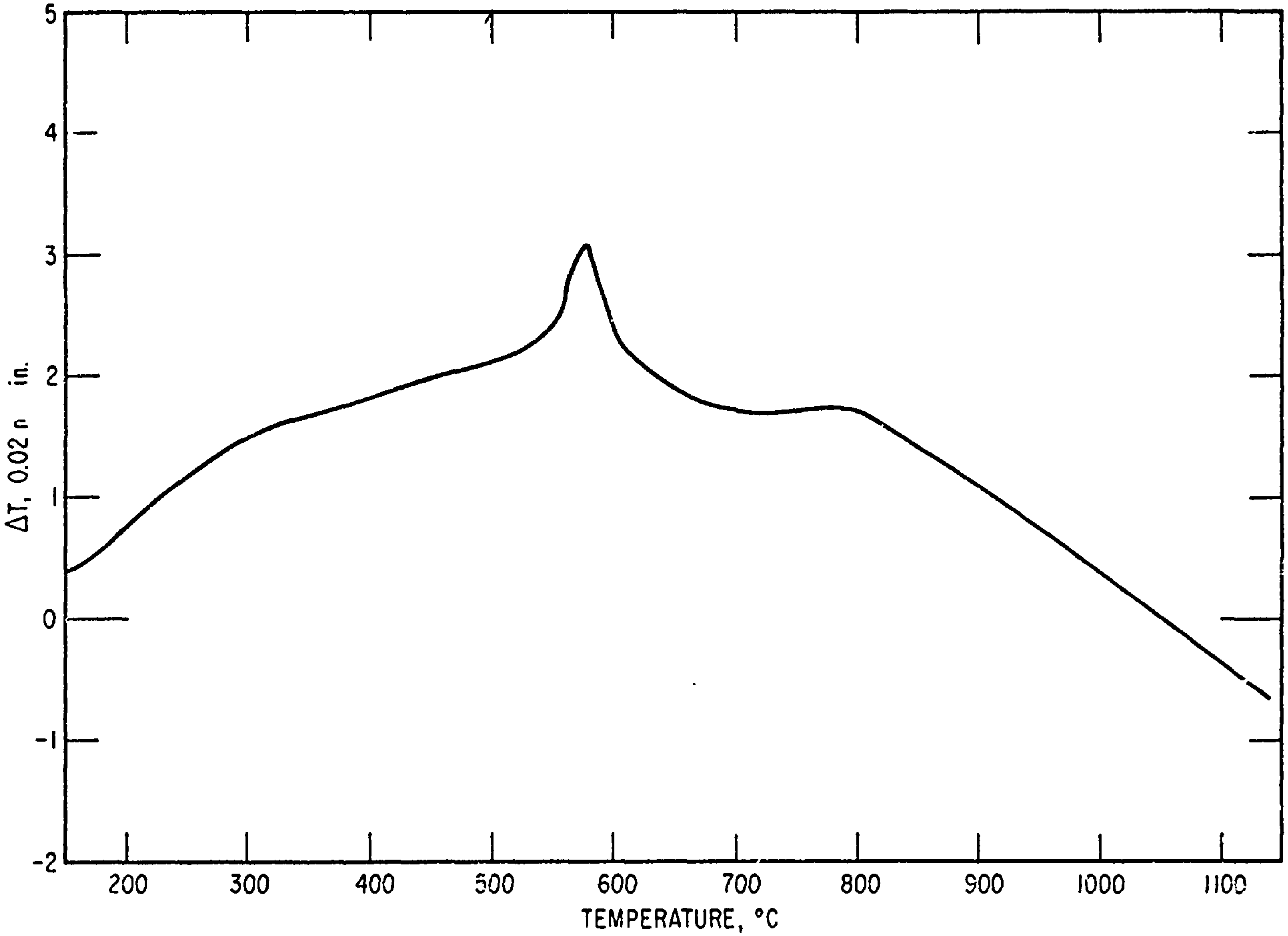


Fig. 15. DTA Curve in Vacuum for Polymer III

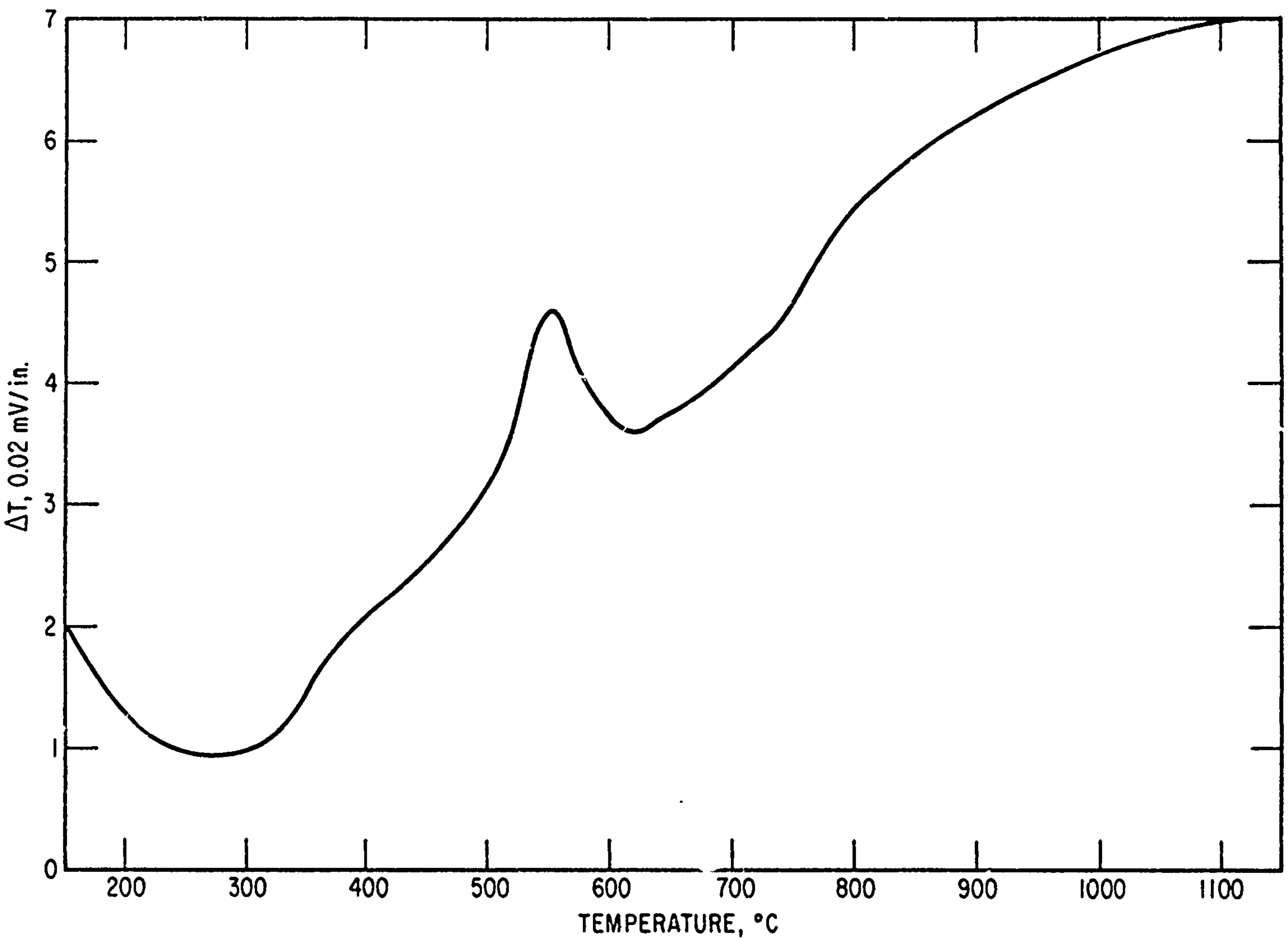


Fig. 16. DTA Curve in Vacuum for Polymer IV

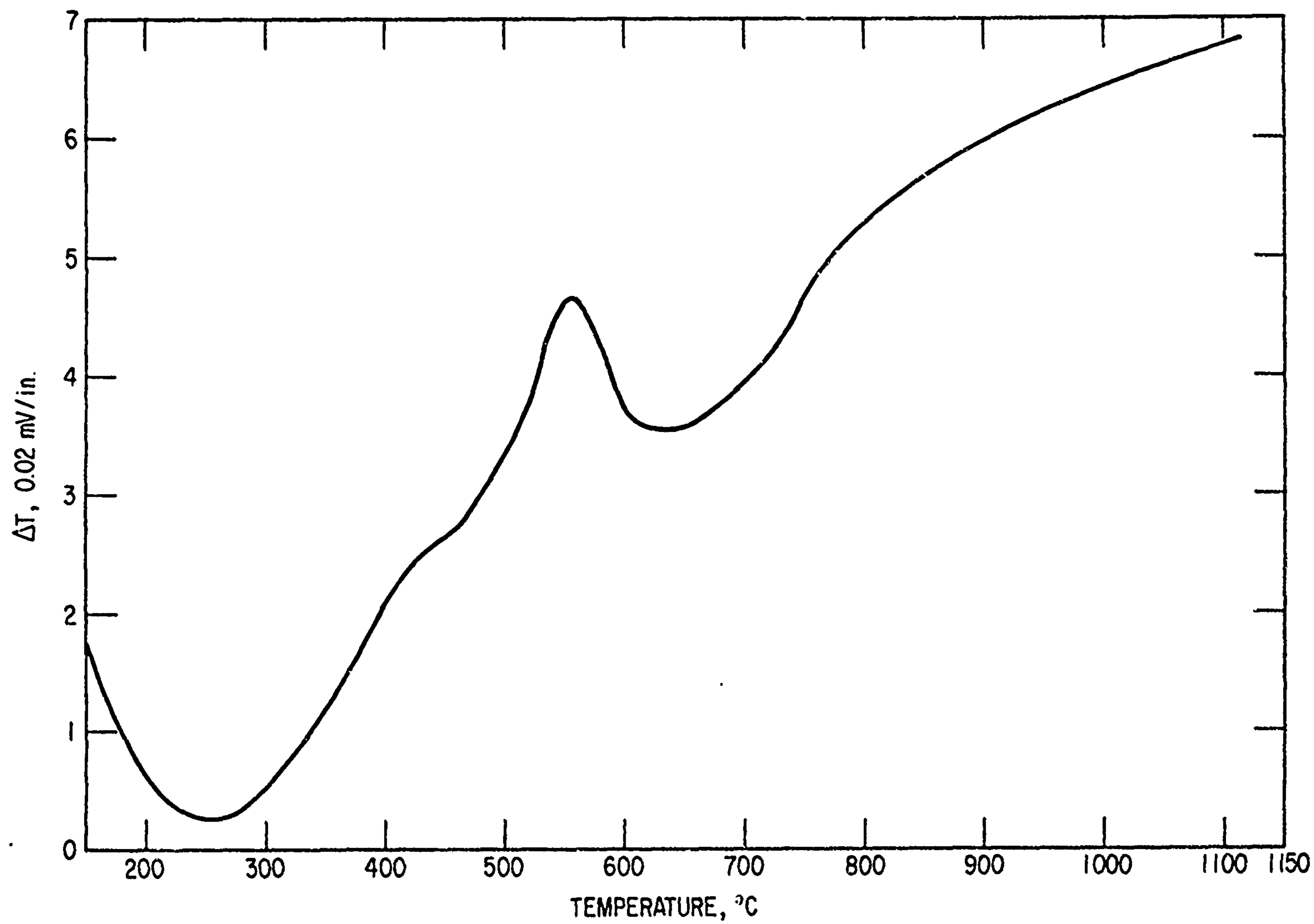


Fig. 17. DTA Curve in Vacuum for Composite

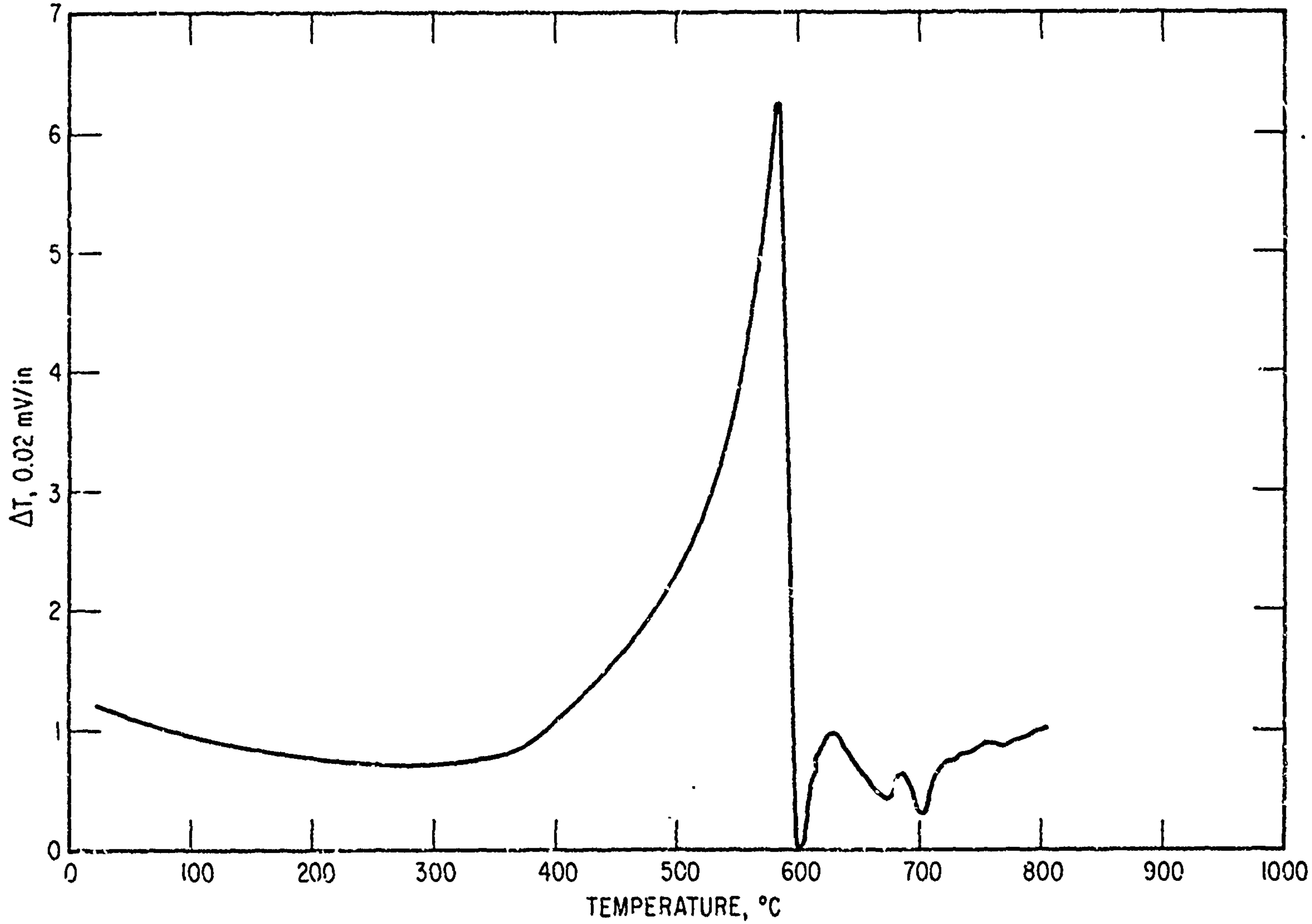


Fig. 18. DTA Curve in Air for Polymer I

temperature, since the bulk of the evolved gases is removed from the cell through this path. This measurement does not permit a direct quantitative estimation of the evolved species due to sizable differences in vapor pressures and/or pumping speed for widely differing gases and vapors. Nevertheless, as will be seen, certain correlations exist between this and the other measurements obtained.

The pressure curve obtained for decomposing Polymer I is shown in Fig. 19. The principal features of this recording are: a sharp increase in pressure beginning at 550°C, an unresolved peak in the vicinity of 625°C, a larger peak at 735°C, and a third peak at 1025°C. The initial pressure rise corresponds closely to both the DTA peak and the TGA maximum weight loss. The second and third peaks correspond to secondary degradation mechanisms, which will be discussed as the mass spectral data are considered. The pressure responses of Polymers II, III, and IV are shown in Figs. 20, 21, and 22, respectively. These curves are remarkably similar to the Polymer I curve and indicate a close correspondence in the degradation process of the discrete steps that are characteristic of each of the polymers. Similar results are obtained for the composite, whose pressure curve for degradation is shown in Fig. 23.

The mass spectrometric results of these analyses are presented in detail in an Appendix to this report (Tables A-1 through A-12). Simplified interpretations of the spectral analyses are given in Figs. 24 through 28.

In the case of the linear phenyl substituted form, Polymer I, the major volatile degradation products are the following:

1. Benzene (m/e 78) and toluene (m/e 91) are by far the predominant species, peaking in concentration at about 565°.
2. Benzonitrile (m/e 103) also occurs in substantial quantity at this temperature.
3. Much small quantities of as yet unidentified higher molecular weight species also occur at this temperature.
4. A modest quantity of methane (m/e 16) peaks here.
5. A significant quantity of a series of 50 peaks (m/e 50, 51, 52) occur at this temperature; their identity will be discussed later.

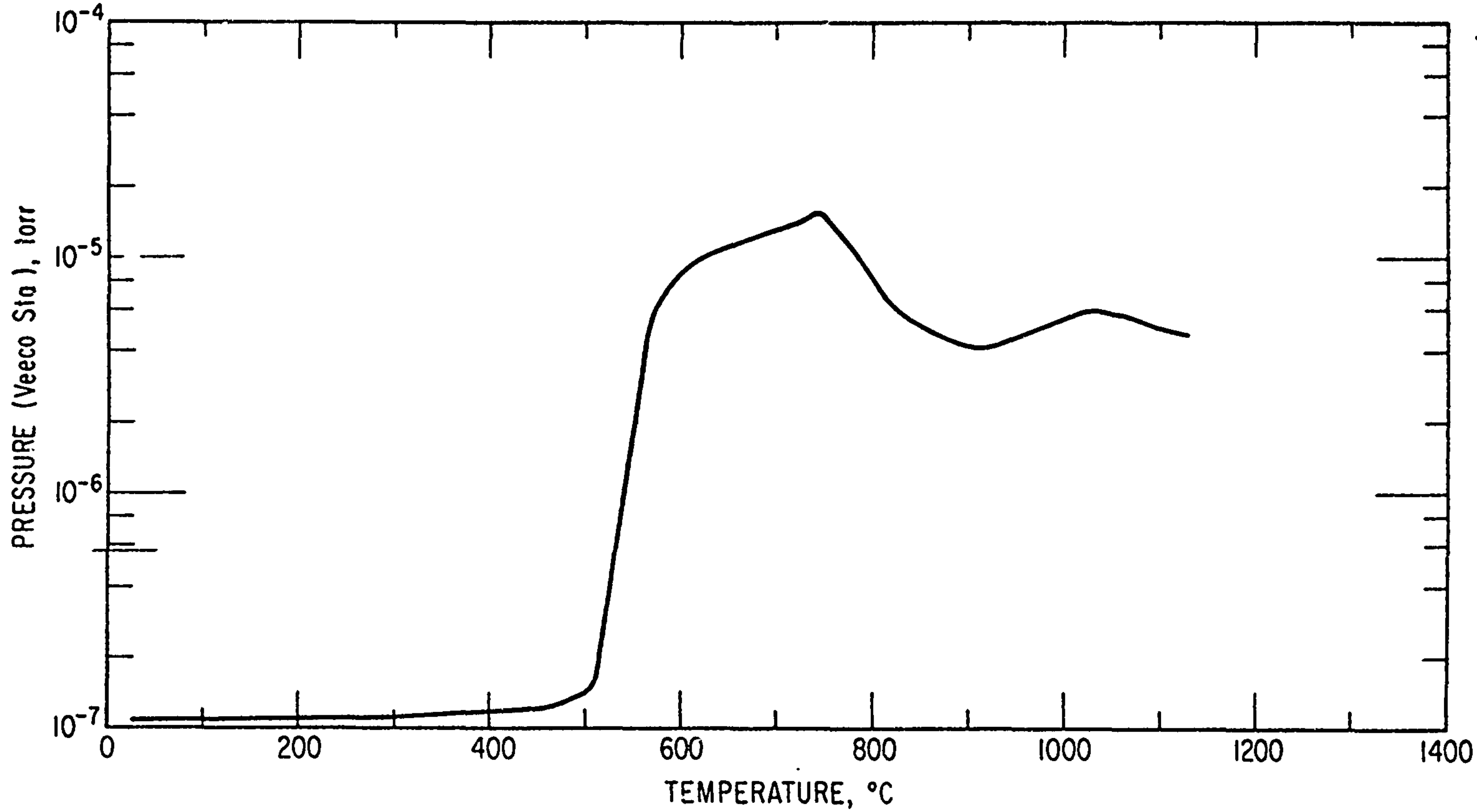


Fig. 19. Thermobarometric Analysis of Polymer I

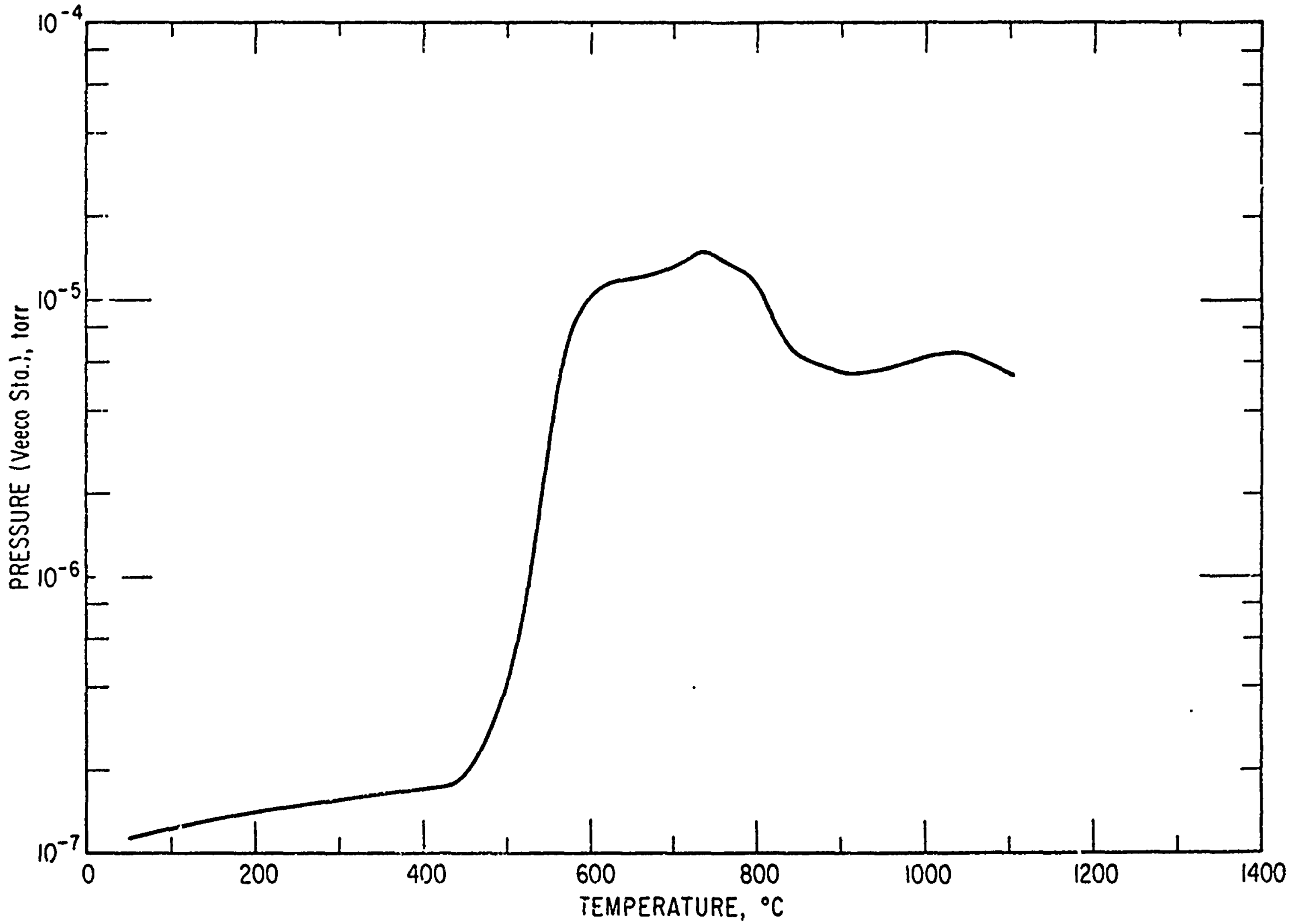


Fig. 20. Thermobarometric Analysis of Polymer II

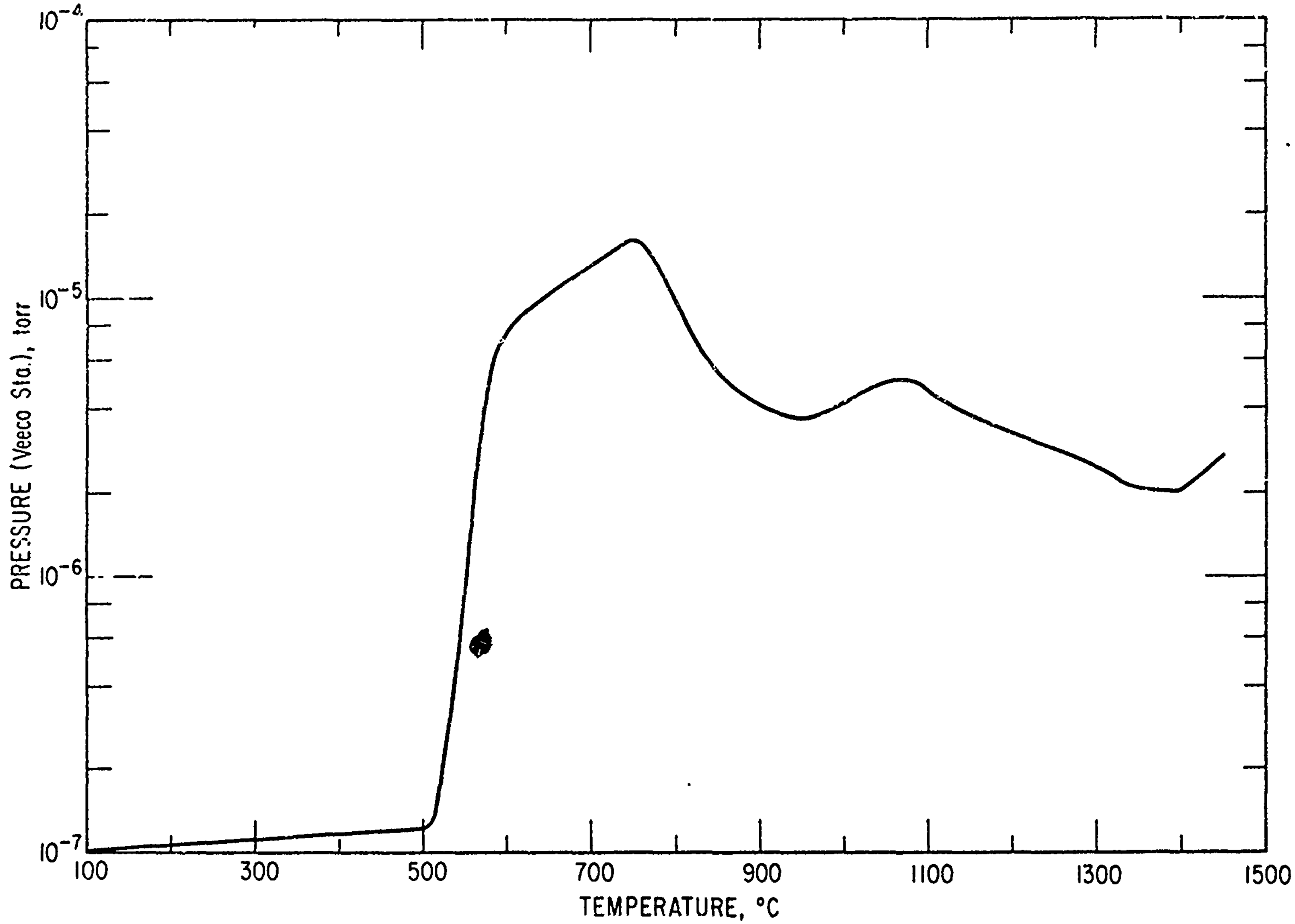


Fig. 21. Thermobarometric Analysis of Polymer III

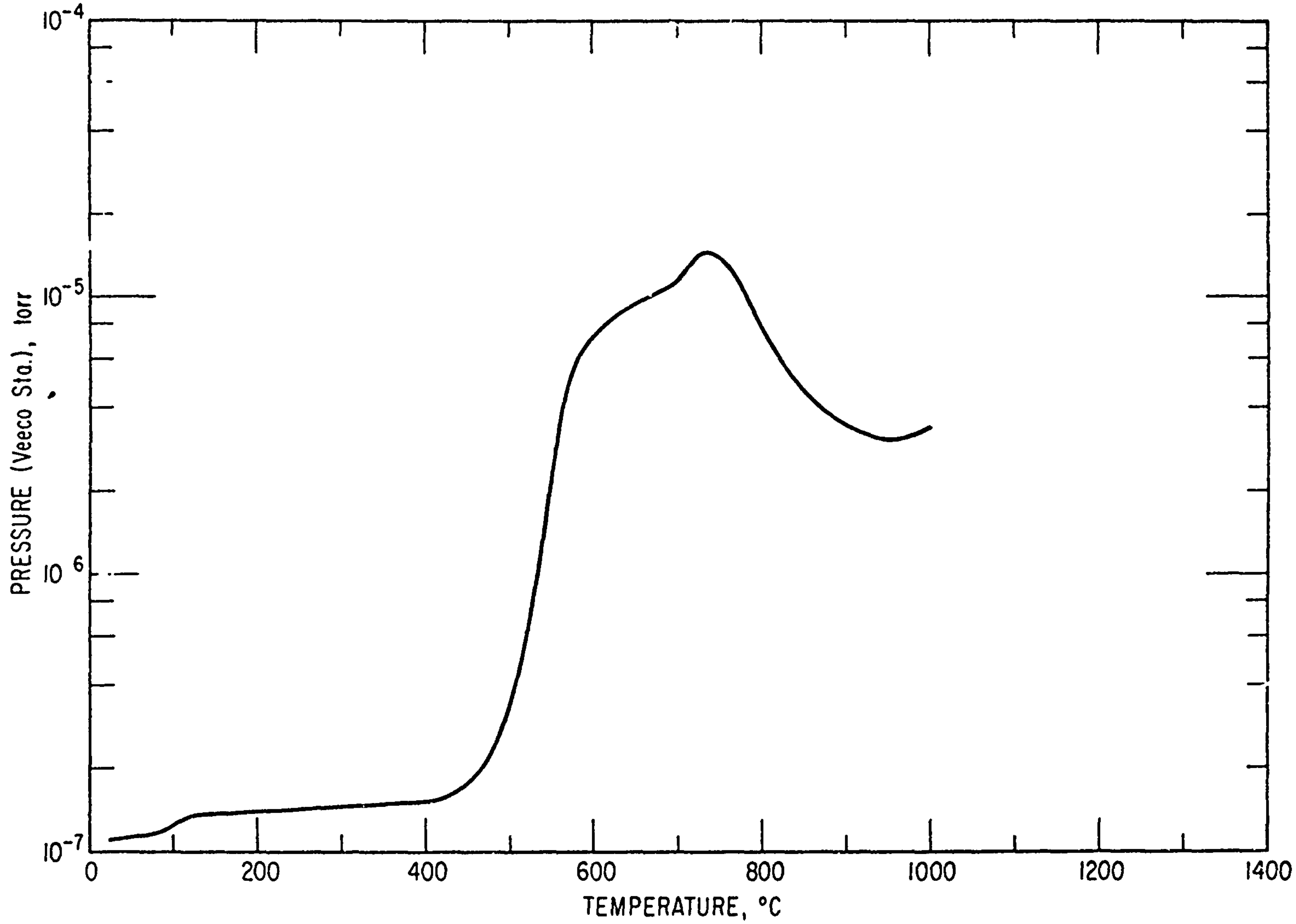


Fig. 22. Thermobarometric Analysis of Polymer IV

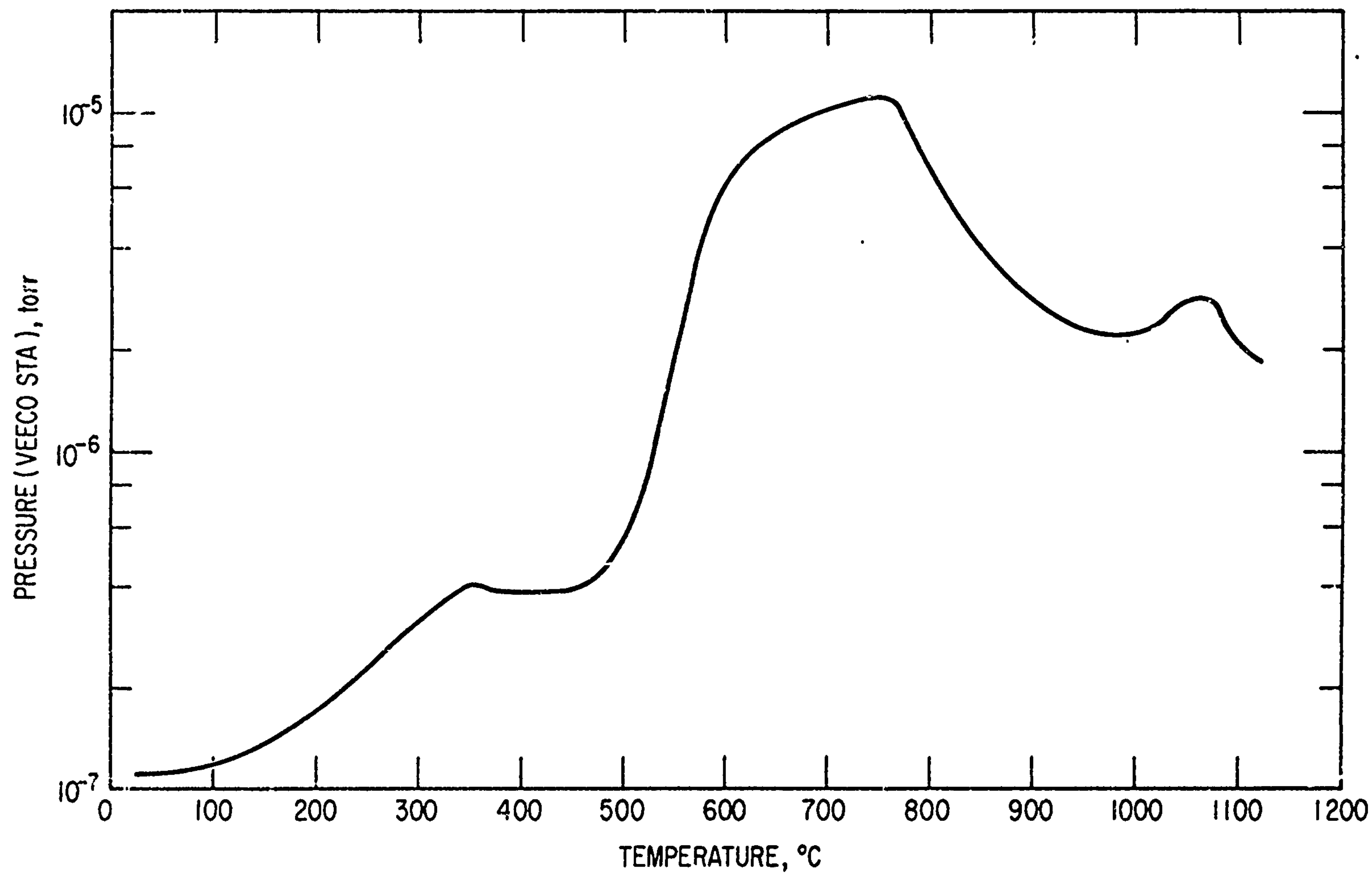


Fig. 23. Thermobarometric Analysis of Composite

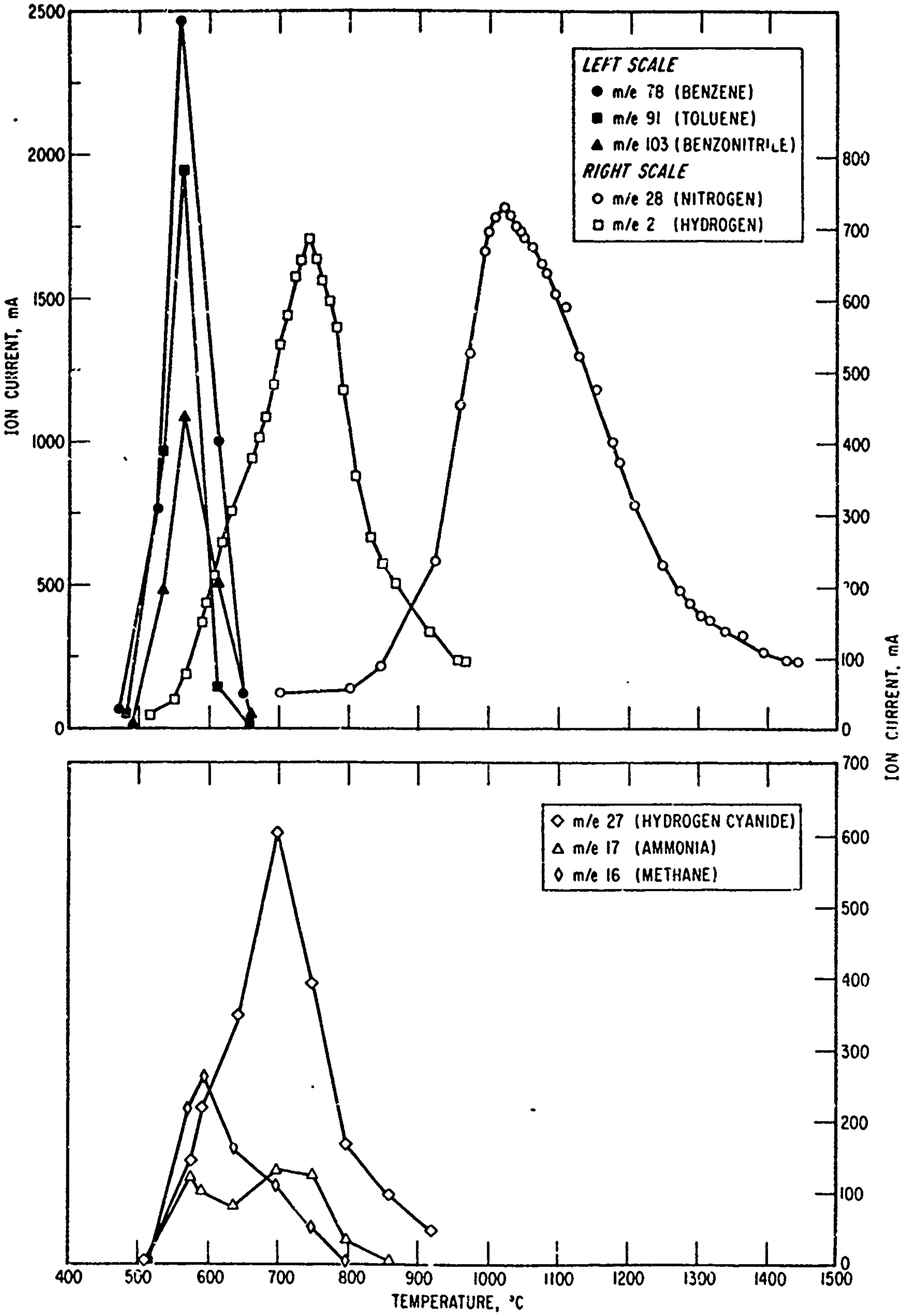


Fig. 24. Mass Spectrometric Decomposition Product Analysis for Polymer I vs. Temperature

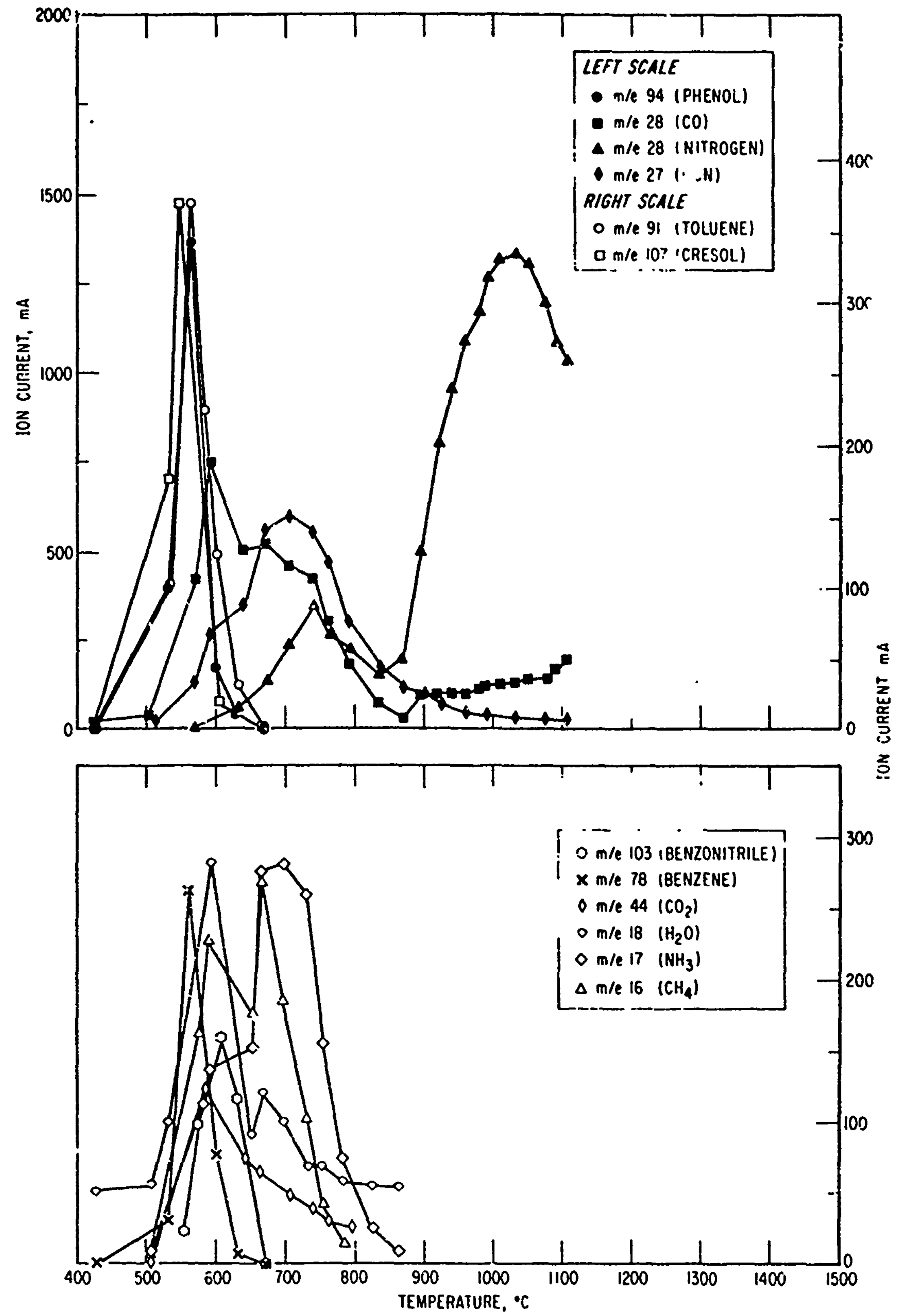


Fig. 25. Mass Spectrometric Decomposition Product Analysis for Polymer II vs. Temperature

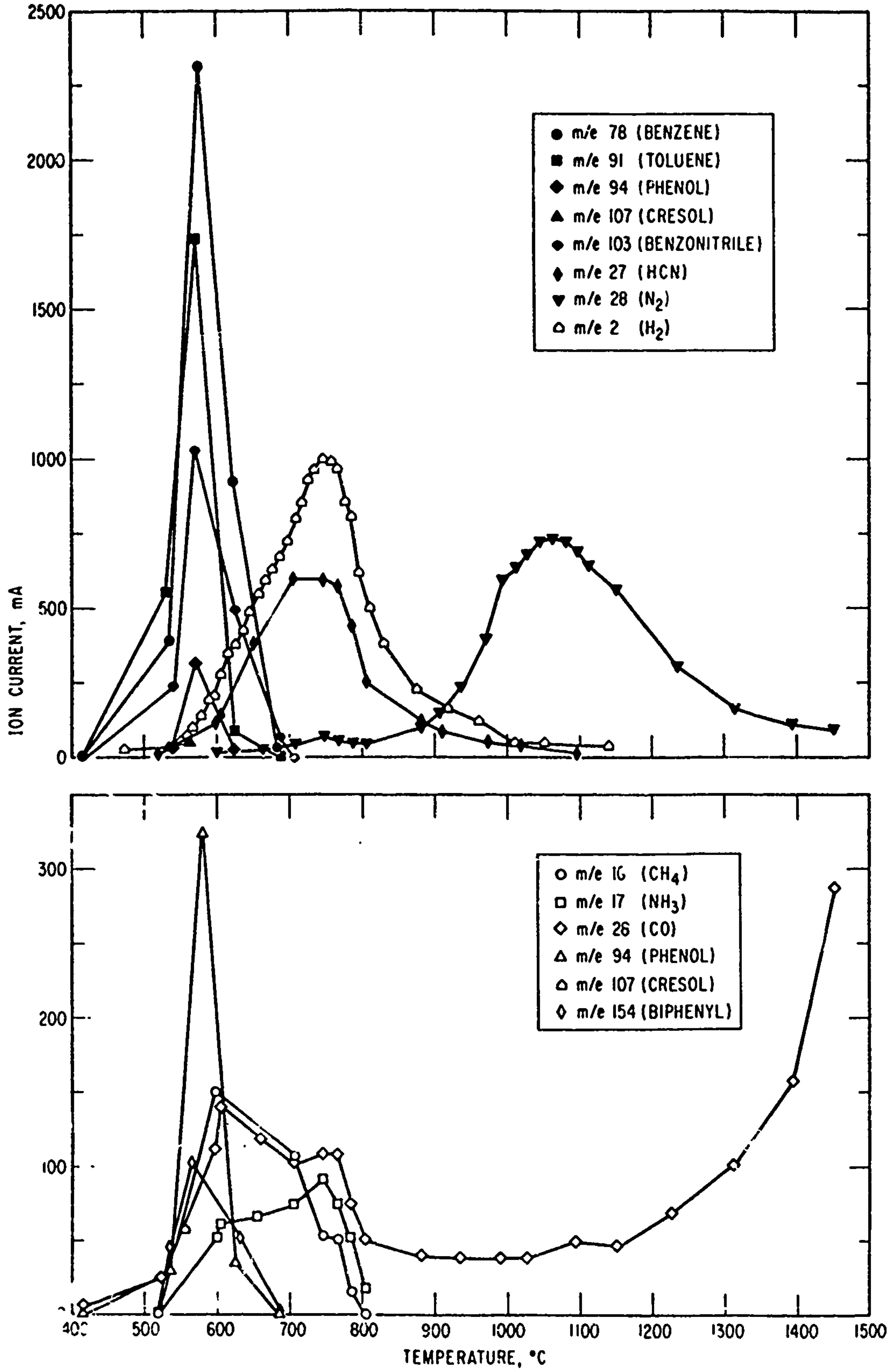


Fig. 26. Mass Spectrometric Decomposition Product Analysis for Polymer III vs. Temperature

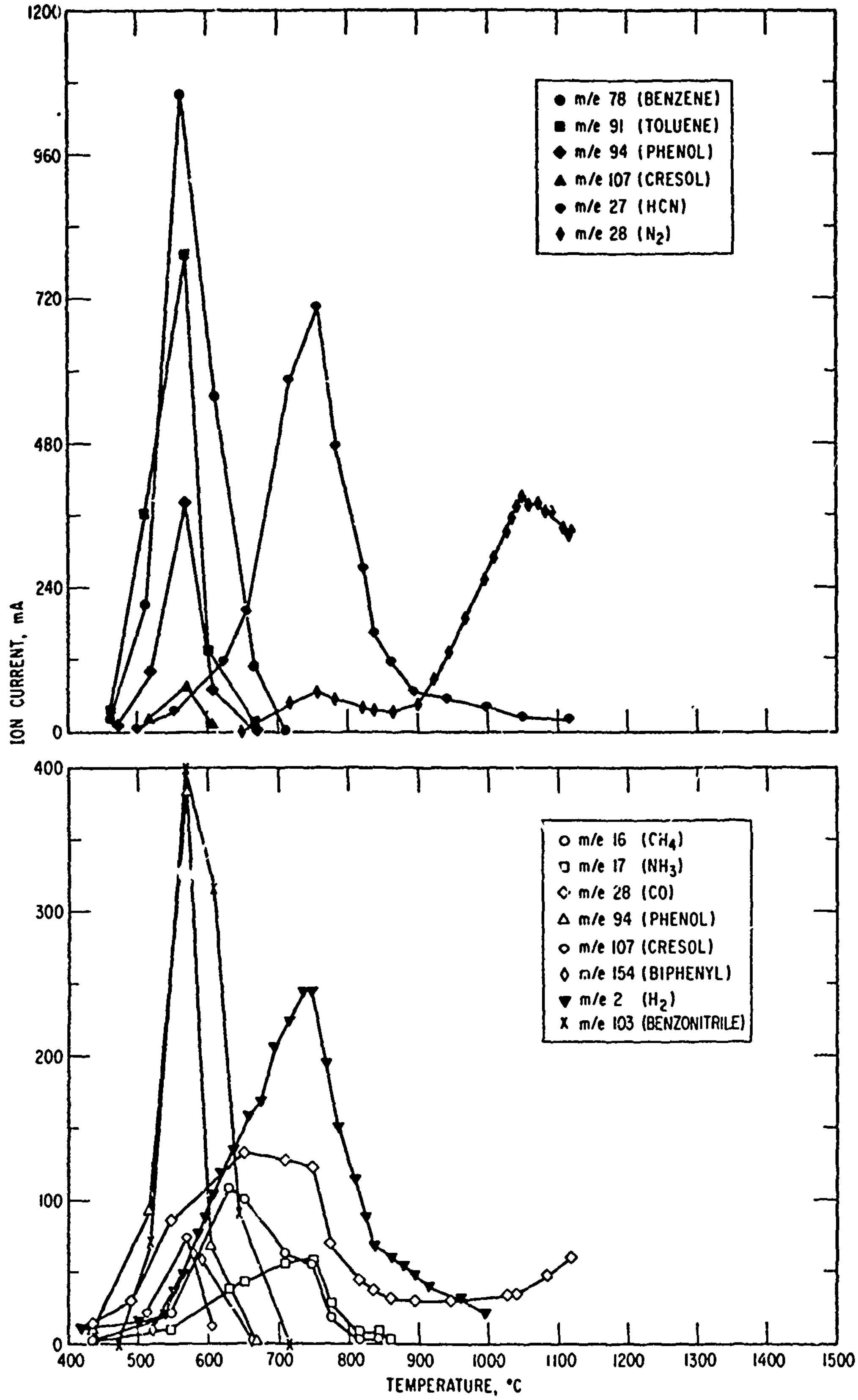


Fig. 27. Mass Spectrometric Decomposition Product Analysis for Polymer IV vs. Temperature

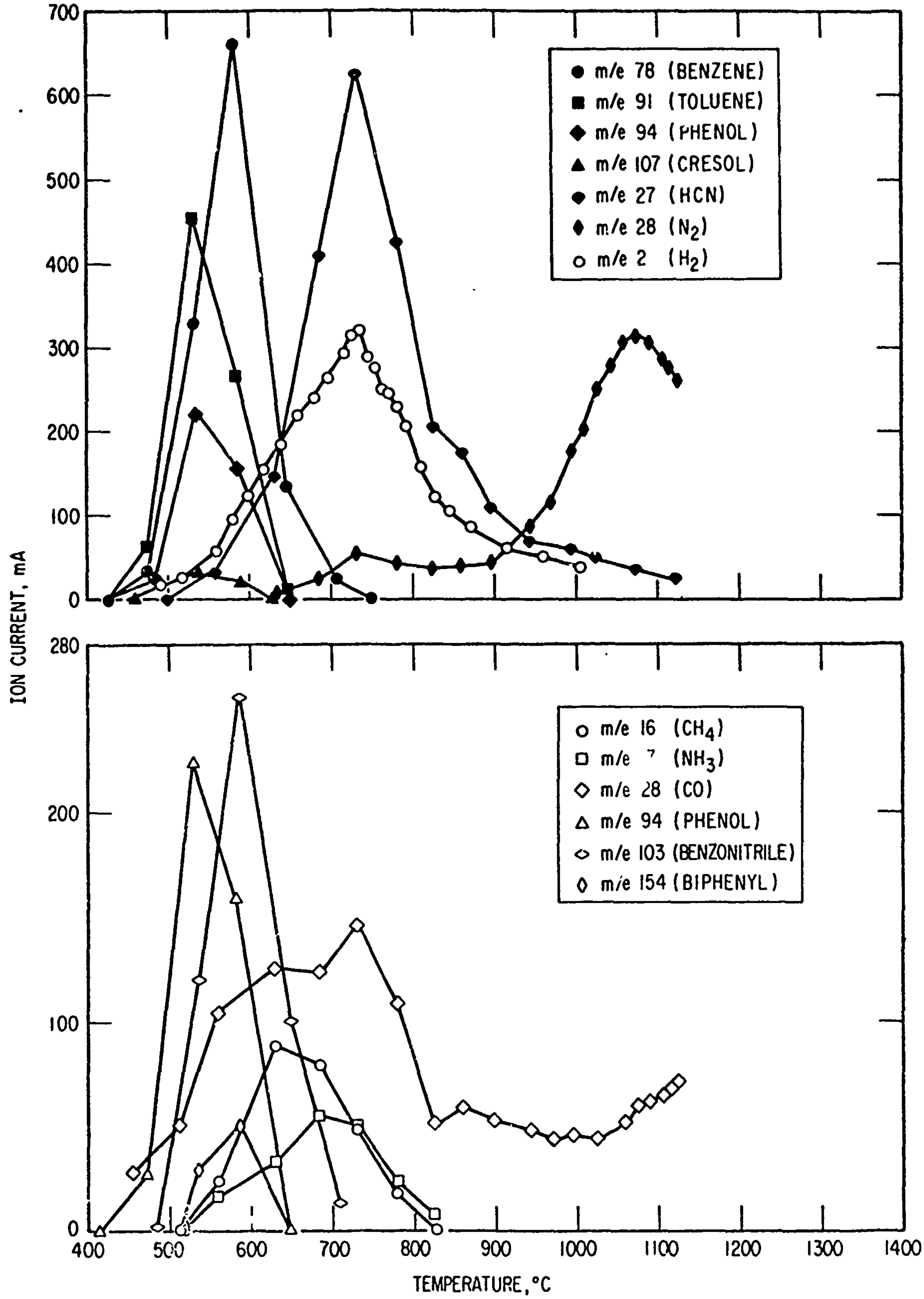


Fig. 28. Mass Spectrometric Decomposition Product Analysis for Composite vs. Temperature

6. At higher temperatures, significant quantities of NH_3 (m/e 17) and HCN (m/e 27) were recorded peaking at 725°C.

7. Sizable quantities of N_2 (m/e 28) occur between 900 and 1100°C, peaking at 1025°C (it is notable that above 900°C nitrogen is the only species detected in significant quantity).

In order to enhance the detection of the principal (aromatic) decomposition products, a similar experiment was carried out in which the spectrometer conditions were fixed to limit the scan to mass 70 and above. In addition, more frequent scans were recorded in the temperature range of maximum decomposition. This experiment resulted in locating the decomposition temperature at more nearly 575°C. It also revealed small quantities of tolunitrile (m/e 117) and probably biphenyl (m/e 154). Smaller quantities of higher molecular weight products, which are as yet unidentified, were also detected up to m/e 206. This experiment was terminated at 700°C, since previous experience indicated that such products could not be expected at a higher temperature. The data from this experiment are given in Table A-3. The results do not significantly alter the summary presented in Fig. 19.

As a result of these experiments, it is possible to assign the cause of the primary weight loss determined by TGA, the exothermic DTA peak, and the initial pressure increase to a decomposition reaction yielding chiefly benzene, toluene and benzonitrile.

The complete absence of high molecular weight species in the degradation product spectra at temperatures above about 900°C suggested that it would be neither desirable nor productive to continue to scan magnetically the entire range of the spectrum at very high temperatures. Consequently, the convention was adopted to limit the mass range covered, initially to m/e 12 to 28, and in later experiments to revert to electrostatic scanning with higher resolution of the m/e 27-28 range. This procedure provided the potential for rapidly recording the varying production of HCN, CO, N_2, and C_2H_4. The results for Polymer I of the modified high-temperature analysis are given in Table A-2. This table is the source of the data for nitrogen plotted in the summary (Fig. 24). Nitrogen is seen to peak at 1020°C. (Carbon monoxide and ethylene were resolved and recorded in this experiment, but

these did not turn out to be significant). Evolution of nitrogen alone, then, accounts for the pressure peak above 1000°C and for the resumption of weight loss in the TGA curve above 950°C.

Instrumental limitations in mass spectrometry dictate that different operating conditions be employed for analysis in the low mass range. Consequently, for monitoring hydrogen production in the degradation process, a separate experiment was carried out using repeated electrostatic scanning with the spectrometer focused specifically at m/e = 2. The data from this experiment are also included in Fig. 24, which shows that hydrogen production is most intense at 735°C and is essentially complete at 950°C, just prior to the temperature where nitrogen evolution becomes significant.

The above result shows that evolution of hydrogen together with HCN and NH_3 (mentioned earlier) are responsible for the second dip in the TGA curve as well as the second pressure peak. The processes whereby these products evolve are not, however, associated with either exothermic or endothermic reactions, insofar as can be detected.

Similar series of mass thermal analyses were carried out for the other polymers included in this study as well as the composite. Detailed analytical results are presented in Tables A-2 through A-12. For simplicity, these have again been summarized in Figs. 25 through 27. These figures relate to Polymers II, III, IV, and the composite, respectively.

Several marked similarities appear in the decomposition patterns. Hydrogen and hydrogen cyanide predominate in the secondary degradation step, while nitrogen evolution is characteristic of the range 900 to 1200°C. The most pronounced differences occur in the primary degradation. In Polymer II, Fig. 25, the phenylene oxide group gives rise to phenol, cresol, and carbon monoxide. The evolved quantity of benzene is sharply reduced, as is benzonitrile, while the quantity of toluene persists. Evidently the phenyl ether group is capable of preferentially inducing primary cleavage in the heterocyclic ring.

Unlike the above, in the crosslinked condition in Polymers III and IV (Figs. 26 and 27), the preponderance of benzene and toluene is restored, and

phenols are strikingly diminished. Carbon monoxide remains a significant but minor product. Benzonitrile reappears as a major product in the primary degradation process.

In the instance of the composite, there exist only quantitative differences relative to the crosslinked polymers. This is expected, because of the lesser quantity of resin in the composite. Qualitatively, no major differences in the degradation process are observed. This result suggests that the reinforcement fiber is inert with respect to the mechanism of thermal degradation of the polymer. It does not, however, rule out the possibility of an inhibitory effect, which could influence quantitative aspects of the reaction and account for the marked difference in char yield reported earlier (see Fig. 5).

Because each of the spectral analyses for the degradation of the polymers contained strong signals for the series m/e 50, 51, and 52, and in view of earlier work (Ref. 11) that suggested the existence of cyanogen ($(CN)_2$; m/e = 52) in the products of degradation, it was deemed desirable to investigate the latter possibility in some depth. Some ambiguity is possible in the assignment of these masses, although it would appear likely that these could be accounted for on the basis of hydrocarbon fragments in view of the very large concentrations of benzene and toluene in the spectra. Nevertheless, consideration should be given to other possible ions such as cyanogen (m/e = 52), even though the fragment ion m/e 26 (CN^+) can be accounted for on the basis of the HCN present. Those ions that could conceivably occur are listed in Table 3.

Although the ions suggested in Table 3 may appear to be rather close in mass, they nevertheless differ by approximately 1 in 5000 amu. Employing the mass measurement capability of the spectrometer, a precise measure of the masses of the three ions appearing in the decomposition spectrum of polyquinoxalines was attempted. The instrument was set at a baseline resolution of 1:5000, a sample of Polymer I was programmed to the onset of the exotherm, and the apparatus was turned to isothermal operation; a small quantity of acetone ($(CH_3)_2CO$, m/e = 58.0418) was introduced as a mass marker. The mass measurement range of the spectrometer extends to

Table 3. Exact Masses of Several Ions

Approx m/e	Ion Formula	Exact m/e
50	C_3N	50.0031
	C_4H_2	50.0156
51	C_3HN	51.0109
	C_4H_3	51.0235
52	C_2N_2	52.0062
	C_3H_2N	52.1037
	C_4H_4	52.0313

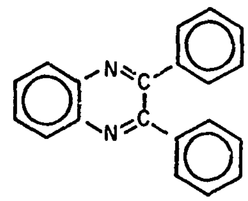
12% of the lighter amu, which permitted measurement between 52 and 58. After measuring mass 52 against mass 58 as a reference, masses 50 and 51 were then determined with the mass 52 used as reference. The masses measured in this way, evolving in the decomposition of the polymer, are listed in Table 4. These results establish, within an average of about 20 parts-per-million, that these masses in the spectra are simply hydrocarbon fragments derived from benzene and toluene. Cyanogen and other nitrogen-containing materials, such as low molecular weight nitriles (with the exception of HCN and benzonitrile), are therefore not decomposition products of polyquinoxaline polymers.

Table 4. Precise Mass Measurement of Species Evolved in Degradation of Polymer I

Approx m/e	Measured m/e	Ion Formula	Calculated m/e	Deviation
50	50.0167	C_4H_2	50.0156	+11/500,000
51	51.0243	C_4H_3	51.0235	+8/500,000
52	52.0321	C_4H_4	52.0313	+8/500,000

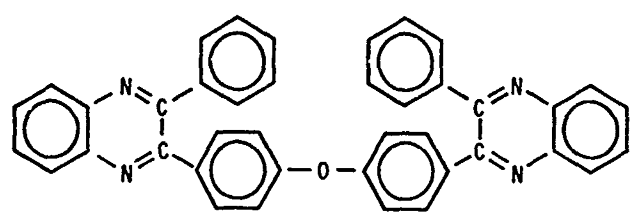
As an adjunct to the thermal degradation studies a pair of model compounds was selected as being appropriate to represent key portions of the linear (I) and crosslinked (IV) polymer. These were, respectively,

1. 2, 3-diphenylquinoxaline*



and

2. 4, 4' bis(3-phenyl-2-quinoxalyl) diphenyl ether**



M. R. -229.5-230.5°C

Because of the appreciable vapor pressures of these model compounds a continuous mass thermal analysis technique was not applicable. Consequently, each material was placed in a special tube adapted to the spectrometer inlet, sealed under 10^{-6} torr, and successively heated at various temperatures until decomposition was observed. At such time a break-seal on the tube was opened and the degradation vapors admitted to the spectrometer source. Degradation was first observed for model 1 at 560°C and for model 2 at 480°. Analysis of degradation products from model 1 yields primarily benzene and hydrogen. On a relative basis about 10% methane is observed, together with traces of ammonia and benzonitrile, but no detectable toluene. In contrast, model 2 yields roughly 4:1:0.2 benzene, toluene and benzonitrile.

*Aldrich Chemical Co., Milwaukee, Wis., No. 14, 548-3

**Kindly supplied by Dick Rafter, Whittaker Research and Development, San Diego, California

Hydrogen and methane are greatly reduced compared to 1, and phenol and cresol are undetected. While these results are not directly comparable to those of the polymers, a certain degree of correlation exists. Hydrogen and methane are explainable on the basis of fragmentation of aromatic products as a result of prolonged residence at temperature. Since the treatment was milder for 2 than 1, these species are greatly reduced. The observed differences in degradation behavior between the models and the polymers are believed to occur because the models are degraded in the vapor state, whereas the polymers are fixed in the solid state.

C. ISOTHERMAL DEGRADATION RATES

In view of the usefulness of degradation rate measurements in analytical models for predicting ablation performance of heat shields and for their sizing calculations, a primary objective of this study was to describe the kinetics of the degradation process for quinoxaline polymers. Initial attempts to accomplish this objective met with limited success.

The experimental approach involved the use of existing thermogravimetry apparatus to determine isothermal degradation rates. The initial experiments were restricted to studying Polymer I. A sample of powdered polymer (ca. 75 mgm) was placed in the apparatus, vacuum applied to 10^{-4} torr, and the furnace activated to heat at its maximum rate from ambient to the desired temperature. Sample weight was continuously monitored. The objective isothermal temperatures were selected to bracket both the primary and secondary mass loss mechanisms. It turned out, however, that the apparatus was not particularly suited to this type of measurement, primarily because of a sizable delay in furnace heat-up, and, in some instances, an undesirable overshoot in temperature. The experiments were carried out to sufficiently long times to indicate the high degree of long-term stability of the quinoxaline polymer at elevated temperatures. They are also useful in confirming the anticipated char yield as observed in constant heating rate TGA. Results of this series of experiments are presented in Figs. 29 through 34. It is apparent from these curves that excessive heat up time and consequent premature weight loss of the sample invalidate all but the three lowest temperature experiments. Fortunately, these were selected to encompass the primary decomposition mechanism and useful rate data have been extracted. The limitations of the experiment dictate that the preferred rate value be taken as the maximum rate of weight loss in each case. Also, the small number and scatter of the usable data points does not warrant a comprehensive analysis of the data. With these considerations in mind, an Arrhenius plot was constructed (Fig. 35) and a straight line merely eyeballed between the data points. The slope of the line gives a crude value for activation energy of 58 K cal/mol

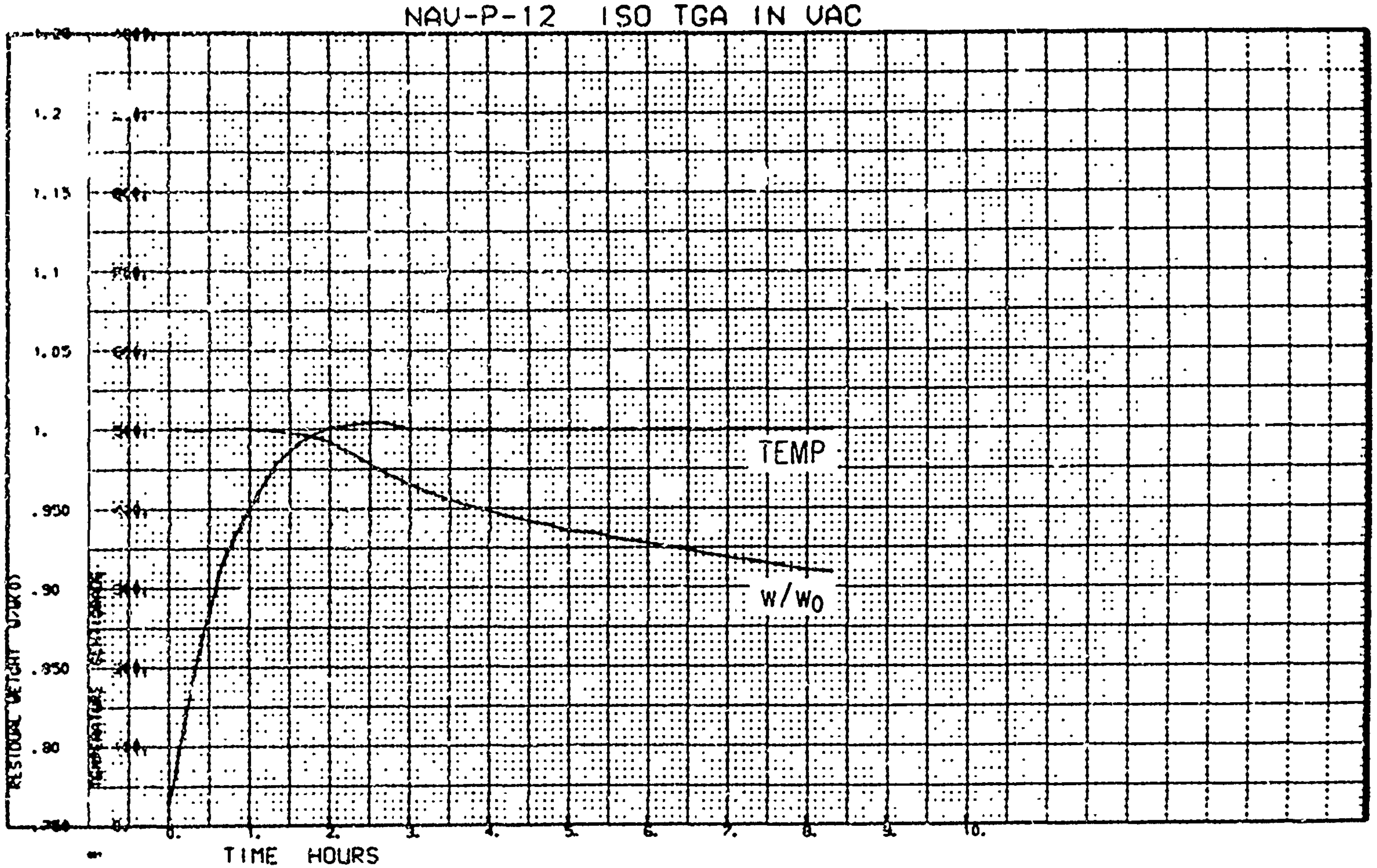


Fig. 29. Isothermal Weight Loss of Polymer I in Vacuum at 500°C

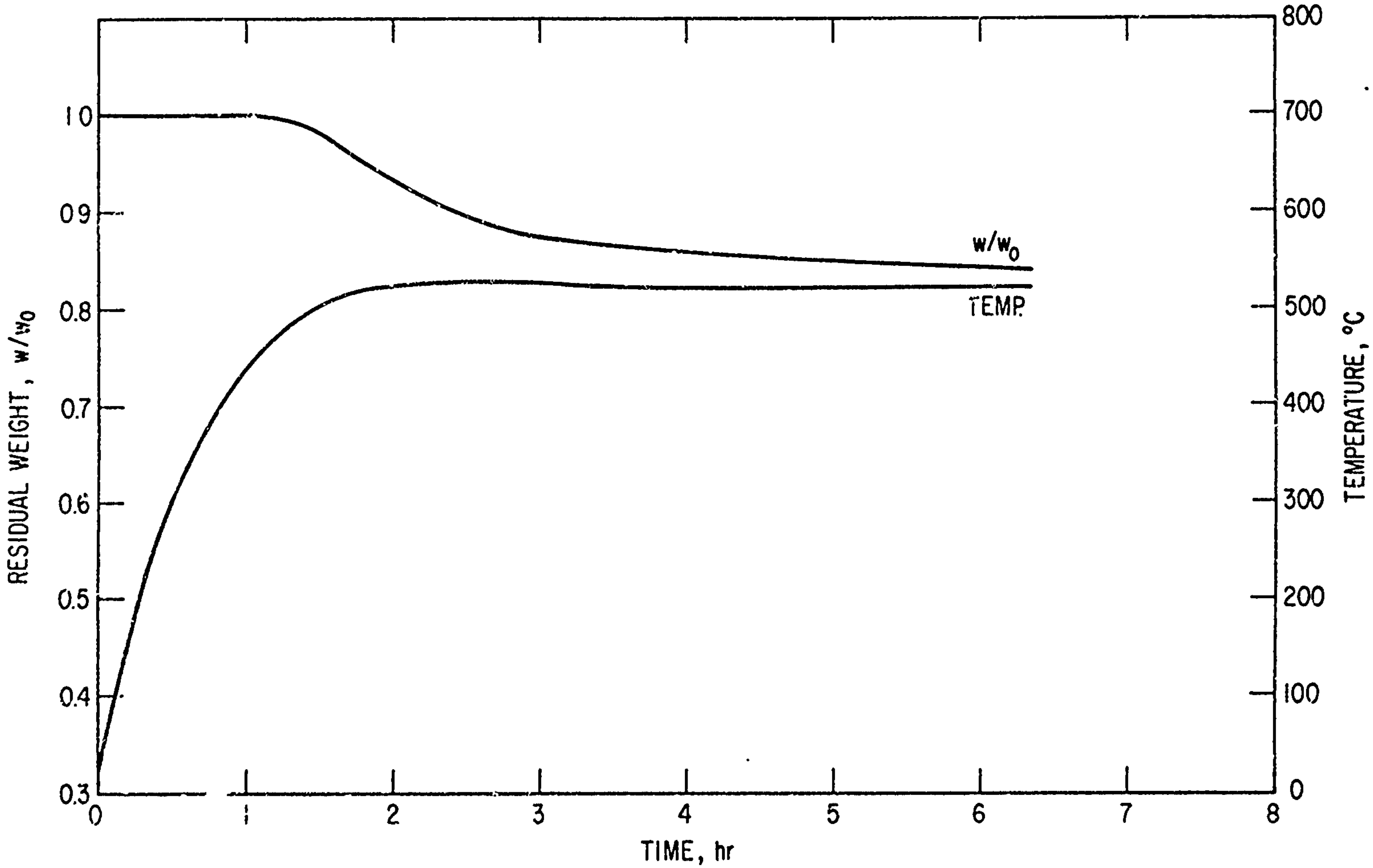


Fig. 30. Isothermal Weight Loss of Polymer I in Vacuum at 525°C

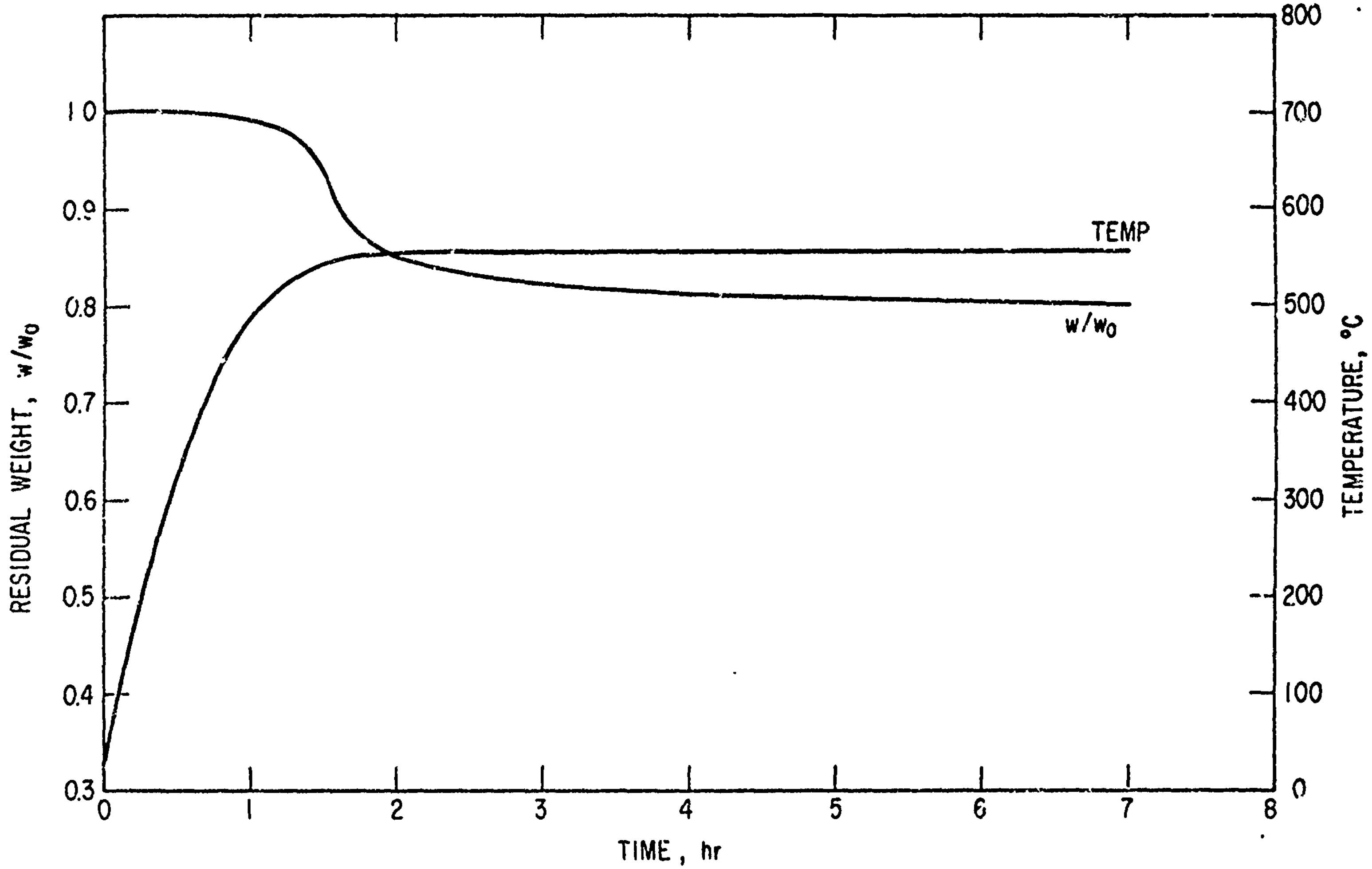


Fig. 31. Isothermal Weight Loss of Polymer I in Vacuum at 550°C

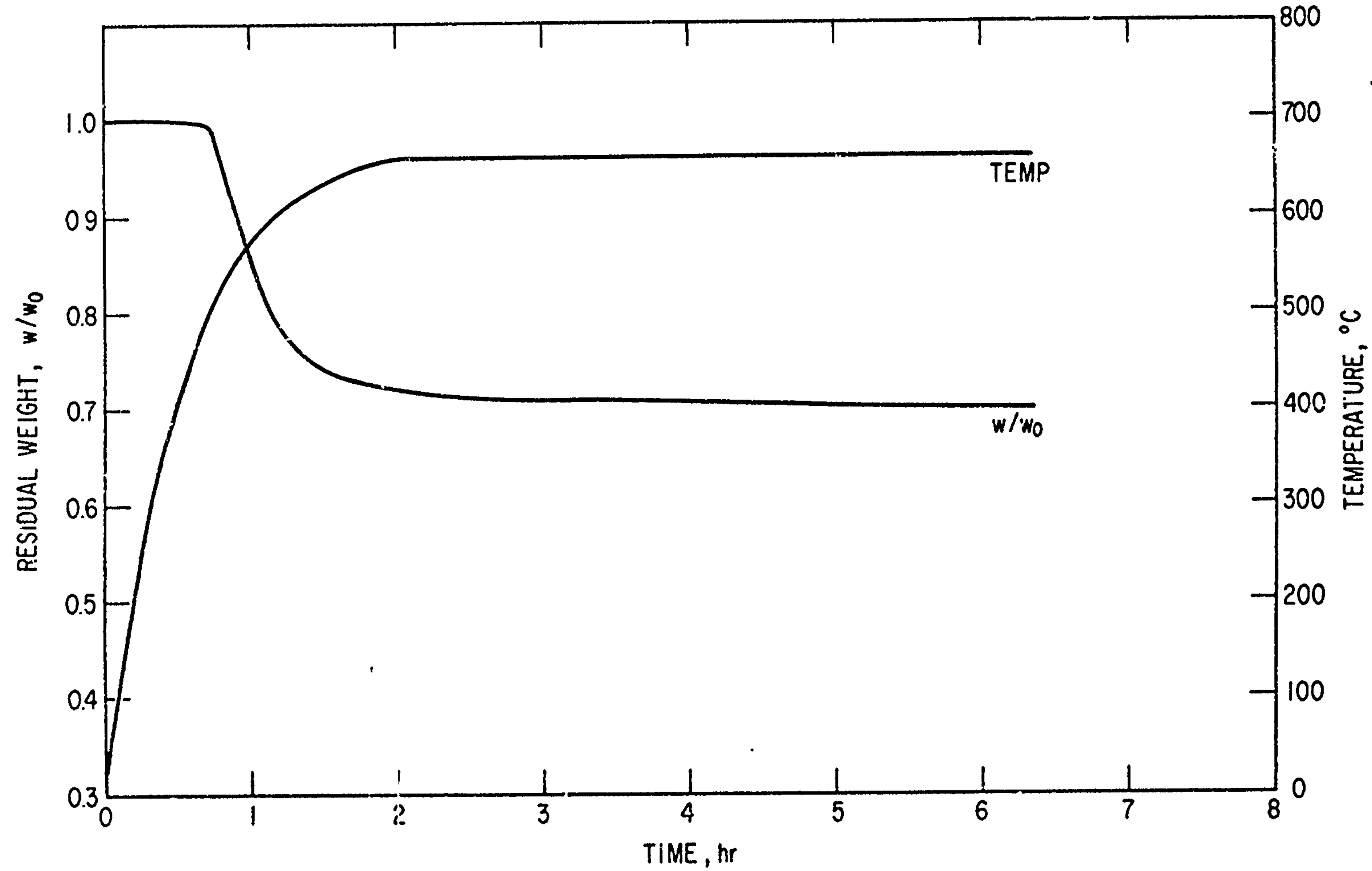


Fig. 32. Isothermal Weight Loss of Polymer I in Vacuum at 650°C

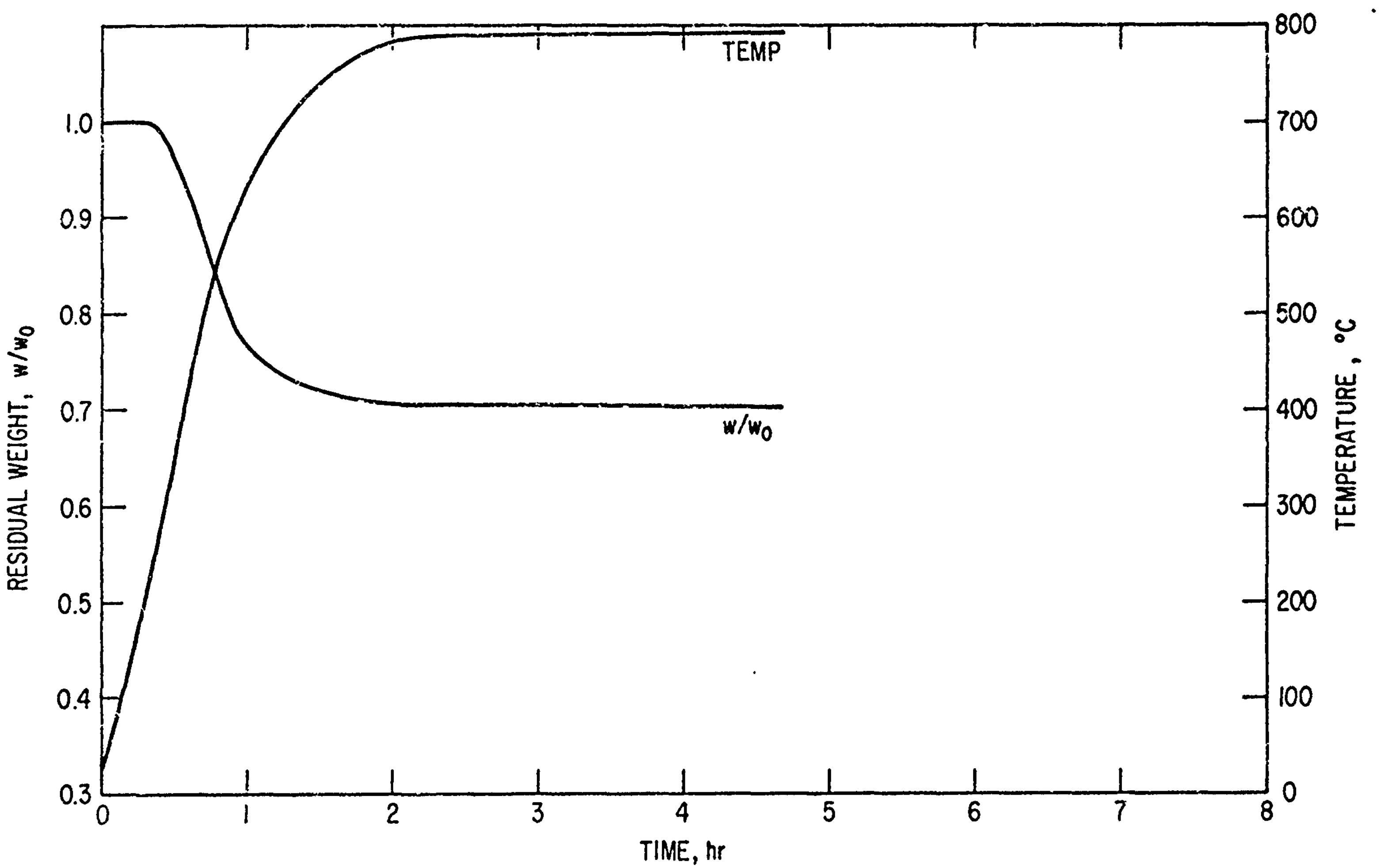


Fig. 33. Isothermal Weight Loss of Polymer I in Vacuum at 800°C

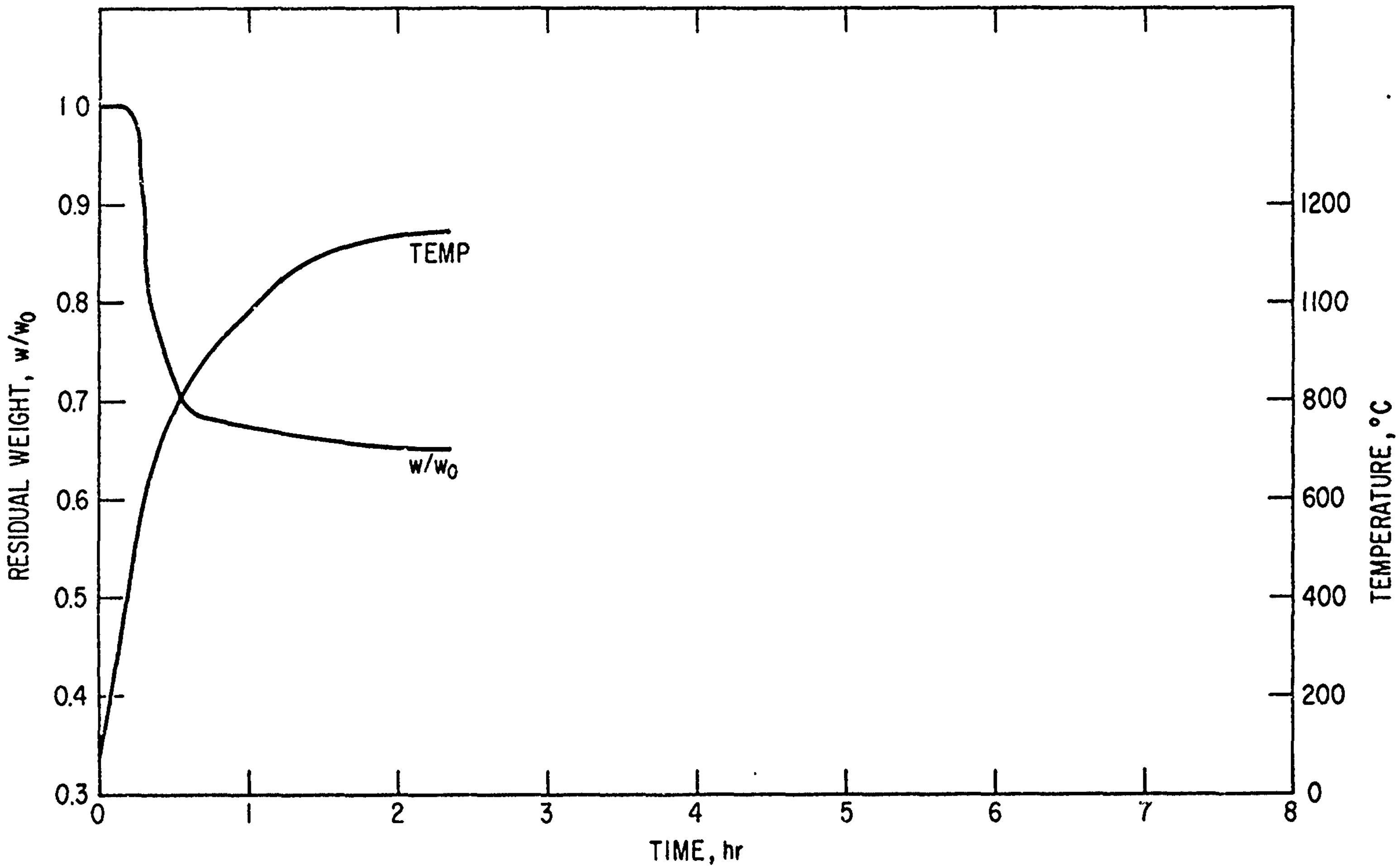


Fig. 34. Isothermal Weight Loss of Polymer I in Vacuum at 1100°C

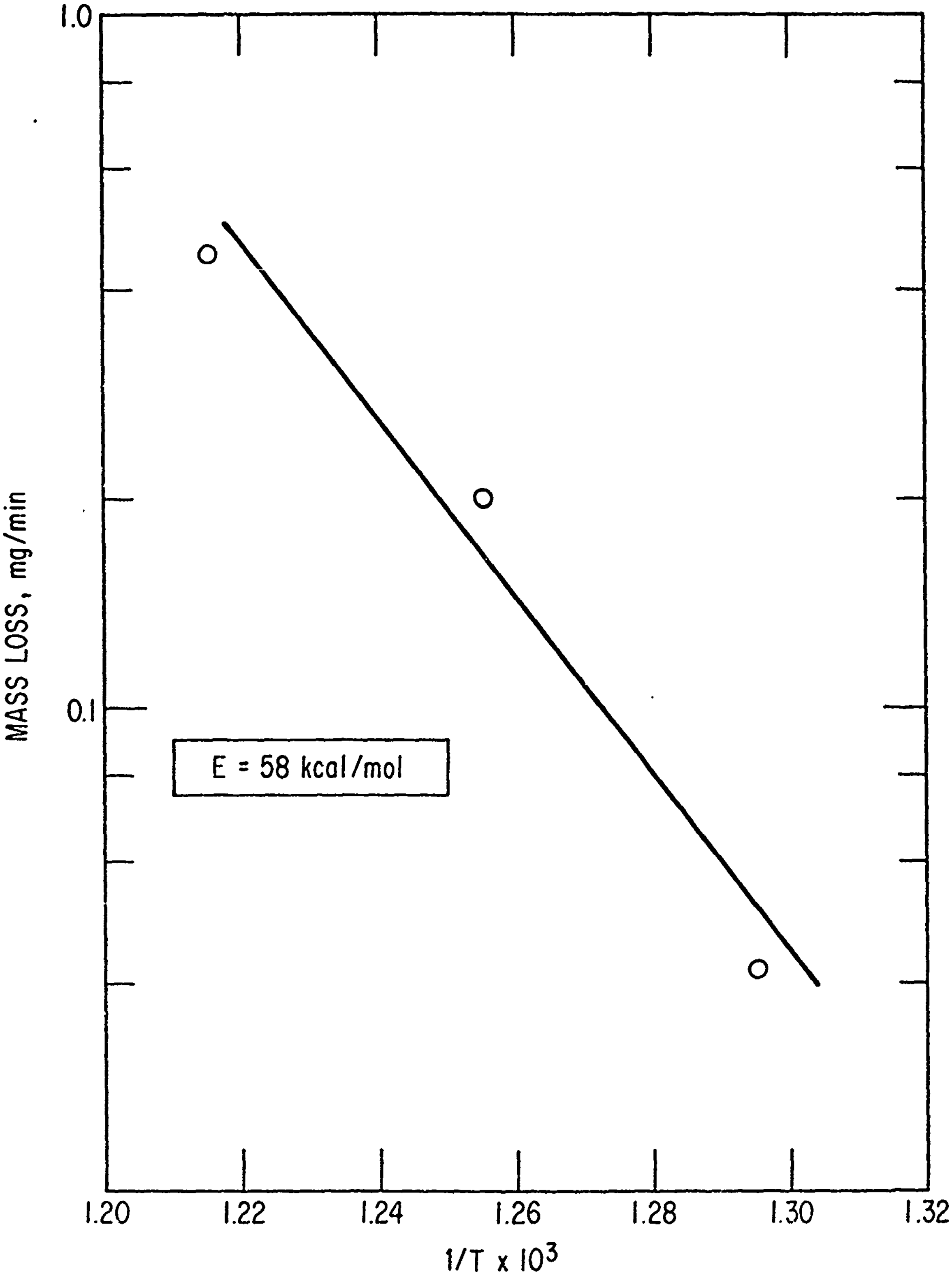


Fig. 35. Arrhenius Plot for Degradation of Polymer I in Vacuum

for the primary degradation process for Polymer I, a value which is in reasonable agreement with previous studies (Ref. 11, 13).

The obvious deficiencies of the experimental approach and crudity of the data strongly suggest that some improvements are needed. An apparatus is needed in which the polymer can be heated nearly instantaneously to the required isothermal temperature. Additionally, since the polymer exotherms strongly during degradation, sample quantity must be restricted and heat dissipation to the environment improved. These modifications to the equipment and technique were anticipated some time ago. At that time, a new apparatus was designed which permits advance heating of the chamber to the desired temperature and subsequent introduction of the specimen with no attendant disturbance of the microbalance or other system components. Conceptually, this modification is simple; reduction to practice involves intricate mechanisms. The change has, however, been successfully accomplished. The equipment has been constructed and performed satisfactorily in shakedown runs. Preliminary DTA experiments have shown that the self-heating effect of the exotherm can be minimized by operating in argon rather than vacuum and by mixing the polymer intimately with a metal heat sink material. In a typical DTA run in Ar, a 1:5 by volume mixture of Polymer I with aluminum powder experiences a temperature increase of approximately 0.3°C on being programmed through the exothermic degradation (Fig. 36). This is a tolerable temperature increase for obtaining accurate rate measurements. A series of isothermal degradation experiments are now in process in which thin films of polymer coated and cured on metal foils are being studied at several well-controlled temperatures in argon atmosphere. Accurate rate measurements are expected from these experiments. As these results become available, they will likely be issued as a supplement to this report.

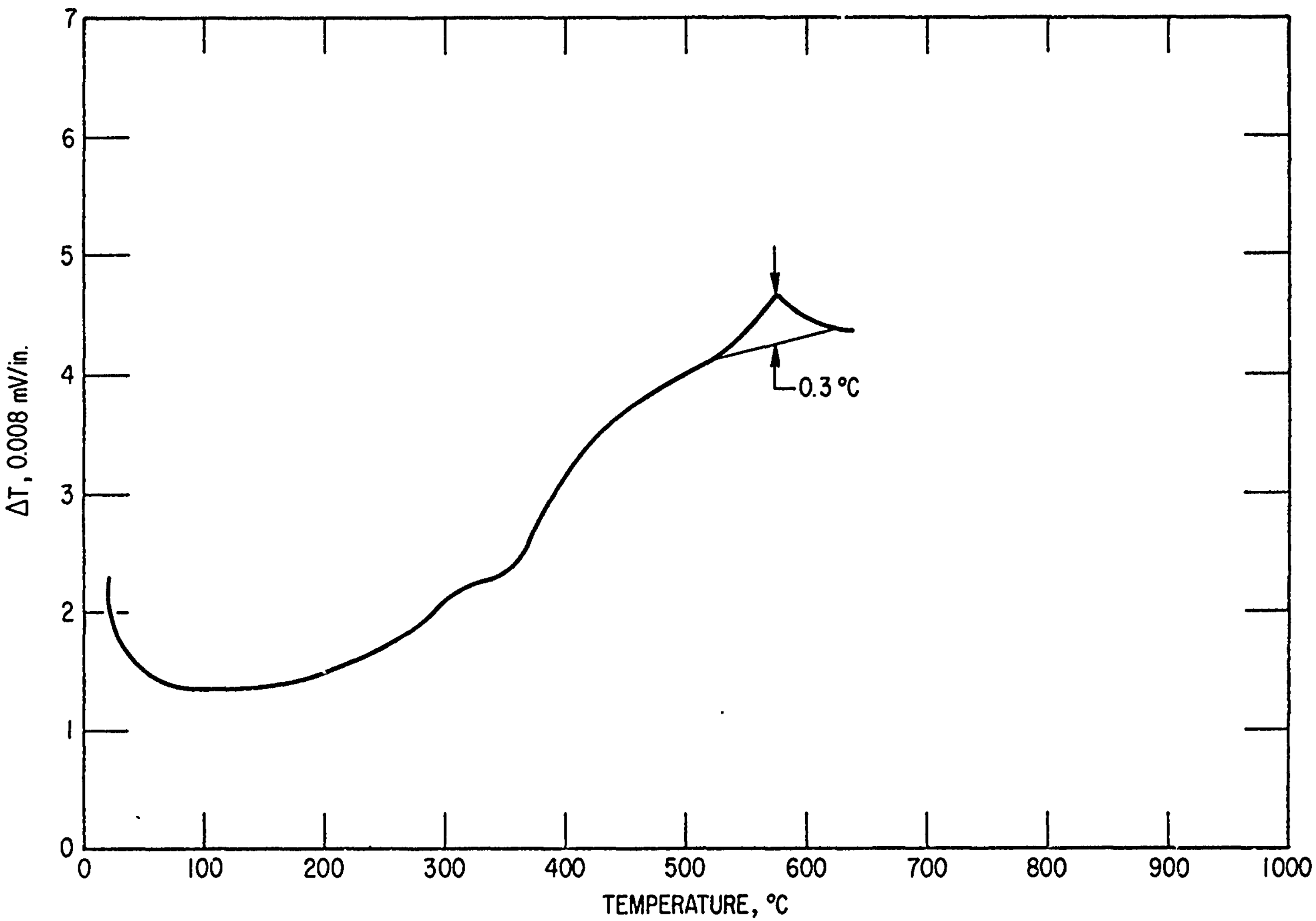


Fig. 36. DTA Curve for Polymer I with Aluminum Powder in Argon

D. RESIDUE ANALYSES

A critical area of analysis, which has largely been neglected in the past, is that of accurate elemental analysis of thermally-prepared polymer residues. As has been demonstrated in this report and elsewhere, the heterocyclic polymers possess extreme thermal stability. One effect of this property is that these materials are inherently difficult to combust and, consequently, they and their intermediate residues are not directly amenable to conventional analytical techniques. A general failure to recognize or appreciate these shortcomings has resulted in the promulgation of much questionable information on the composition of chars, particularly from nitrogen-containing polymers. This state of affairs has severely hampered the ability, in general, to describe degradation mechanisms.

The previous section dealing with mass spectrometry of the degradation products of polyquinoxalines has demonstrated that, under the conditions of the experiments, nitrogen is not completely evolved below 1200°C. In the conventional Dumas analysis for nitrogen the combustion is carried out at 800°C in CO_2 atmosphere. Such conditions are obviously inadequate for complete evolution of nitrogen from these polymers. Our experience has shown that conventional methods do not yield satisfactory mass balances in the analysis of these polymers and their residues. This experience is confirmed in the work of others with pyrolyzed nitrogenous polymers (Ref. 12). Thermogravimetry in air has also demonstrated the extreme resistance of these materials to oxidative breakdown. This situation aggravates the difficulty of obtaining accurate C, H analyses, even though combustion is normally carried out in oxygen.

In view of the need for accurate residue analyses for (1) an understanding of chemical degradative mechanism, (2) a critical analysis of post-ablative test chars, and (3) rational development of carbon/carbon composites it was felt that a certain effort was justified in an attempt to improve the accuracy of these analyses. In this work two approaches have been employed

in an attempt to accomplish this objective. In the first instance the technique of vacuum fusion analysis was applied to a number of known model compounds and to a series of residues. In this method a sample contained in an inert metal foil is quickly introduced into a graphite chamber preheated to 2000-2500°C under vacuum. The sample is intended under these conditions to degrade rapidly and quantitatively to simple molecules which can be readily separated and measured. Oxygen reacts with heated graphite to form CO which is passed over hot copper oxide to convert to CO_2 which is removed by trapping at liquid N_2 temperature. Hydrogen is oxidized over hot copper oxide to H_2O which is scrubbed by magnesium perchlorate. Theoretically only nitrogen remains, and this is measured azotometrically. The analyses of the model compounds by this method proved unsatisfactory because a quantity of condensable degradation products evolved in each case, indicating incomplete sample decomposition. As will be seen, however, the nitrogen analyses of the residues are at least as satisfactory as those obtained by other methods. By a modification that would provide for sweeping the condensables through a combustion train, the method could be applied to the analysis of model compounds as well. Unfortunately this modification could not be tried because the apparatus is the property of another contractor.

The second approach involved an attempt to improve the efficiency of combustion in the Dumas technique. Combustion temperature was increased from 300 to 1000°C. Time of combustion was doubled from ten to twenty minutes and potassium chlorate was added to the sample as a source of oxygen. An appreciable improvement was effected in the analysis as seen in Table 5 which compares conventional and modified Dumas results as well as vacuum fusion results for nitrogen in undegraded Polymer I. It is apparent that a conventional nitrogen analysis is entirely inadequate and that these approaches still leave something to be desired. It is even possible that extreme thermal stability and combustion analysis are mutually exclusive in practice.

The residues from the isothermal degradation experiments were analyzed for carbon, hydrogen and for nitrogen by the two techniques described here. Results of these analyses are reported in Table 6. Material balances are unanimously deficient. Some trends are expected, however, and these are confirmed. From consideration of the mass spectrometric results and the primary mass loss mechanism by loss of benzene and toluene, carbon and hydrogen are expected to decrease initially, while nitrogen increases slightly. Between 650 and 850°C hydrogen and hydrogen cyanide are eliminated, resulting in reduced hydrogen and nitrogen content of these residues. It has been shown that at these temperatures the intermediate chars are highly resistant to thermal and oxidative degradation. This increased stability vitiates against the analysis and consequent material balances are worsened. The greatest decrease in nitrogen content is observed at 1100°C and above, which confirms the mass spectrometry results for this temperature range. At 1350°C residual nitrogen has been reduced 90 to 95% relative to the starting polymer.

Table 5. Elemental Analysis of Polymer I

	C, %	H, %	N, %
Theory	84.28	4.16	11.56
Micro Pregl	83.21	4.38	-
	83.32	4.44	-
Conventional Dumas	-	-	6.50
Modified Dumas[a]	-	-	9.64
	-	-	9.56
Vacuum Fusion	-	-	10.9

[a]Combustion temperature increased to 1000°C; longer residence time; K CLO_3 added.

Table 6. Analysis of Isothermal Residues of Polymer I

Residue Temp, °C	C, %[a]	H, %[a]	N, % Modified[a] Dumas	N, % Vacuum[b] Fusion	Total
500	81.38	4.40	10.68	9.6	96.46-95.38
525	81.06	4.37	10.79	9.8	96.22-95.23
550	80.53	3.62	9.86	10.0	94.01-94.15
650	81.21	2.69	8.77	5.5	92.67-89.40
800	80.33	1.74	7.31	7.9	89.38-89.97
850	81.33	1.62	7.12	7.2	90.07-90.15
1100	88.80	1.00	4.47	4.4	94.27-94.20
1350[c]	97.68	0.24	0.59	0.84	98.51-98.76

[a]Truesdail Laboratories, Los Angeles, Calif.

[b]Courtesy Ann Mongrave, Chemistry Department, Atomics International Div, North American Rockwell Corporation, Canoga Park, California.

[c]Residue from mass-thermal analysis.

E. MICROWAVE STUDIES

Several brief experiments were performed to determine the effect of microwave energy on both uncured and cured high-temperature phenolics. The materials examined were an Ironsides type 101 phenolic and a SC-1008 phenolic manufactured by Minnesota Mining and Manufacturing. Material samples were placed in Al_2O_3 crucibles which in turn were set into an Al_2O_3 firebrick for insulative purposes. All samples were exposed for periods of 3 to 5 minutes in air in a multimode cavity equipped with a mode stirrer. The incident radiation had a frequency of 2450 MHz. The measured power input, as sampled in the waveguide transmission line, was on the order of 600 watts.

The results of these experiments showed the uncured polymer samples to be rapidly cured by the microwave field within the period of exposure time. However, the rapid release of volatile constituents during the short curing cycle resulted in considerable "frothing" of the polymers. However, once cured, no further interaction could be observed with the microwave field. This change of loss characteristics of the polymer was probably due to rapid heating and evolution of moisture from the polymer-i.e., moisture tends to be very "lossy" in a microwave field. However, once the moisture has been evolved, the remaining organic solid has low loss characteristics.

The significance of these observations lies in the potential use of microwaves in rapid, in-depth curing of phenolic structures, such as 3-D carbon-phenolics and quartz phenolics. Obviously, the time scale and power levels in these experiments were inadequate, and it would be necessary to perform additional studies to determine the optimum power-time cycle to cure these materials properly. But the inherent advantage of in-depth heating as opposed to other heating techniques, offers potential benefits such as more complete curing and possibly curing of moderately complex shapes.

III. DISCUSSION AND CONCLUSIONS

As observed from the TGA, the decomposition of polyquinoxalines appears to proceed in three consecutive steps distinguished by plateaus followed by regions of high rates of mass loss. DTA in vacuum detects no endotherms of any signif cance, and a single major exotherm is seen that is associated with the primary degradation step occurring at its maximum rate at 565°C. In this step, about 23% of the polymer's weight is lost in the case of Polymer I, accounting for about 70% of the total mass loss. The principal decomposition products are aromatic hydrocarbons. Step 2 in the decomposition occurs between 650°C and 850°C. This step accounts for an additional loss of 5 wt % of polymer. The volatile products in this step are primarily hydrogen and HCN with lesser amounts of NH_3 and CH_4. The final mass loss process occurring between 850°C and 1400°C, accounting for the last 5% of polymer loss, is principally due to the evolution of N_2.

The above comments are equally applicable to a polymer containing phenyl ether linkages, as well as those crosslinked through phenyl ether groups. Important exceptions to this conclusion are in the quantitative mass losses observed in vacuum thermogravimetry, and in the appearance of phenols and carbon monoxide as primary degradation products. Large quantities of cresol and toluene signal degradative attack in the heterocyclic ring. Quantitative differences are observed between the composite and the corresponding polymer (IV). No qualitative differences are evident.

High-temperature resistance to oxidative degradation of polyphenyl quinoxaline is improved by crosslinking with a trifunctional monomer containing the phenylene oxide linkage. This effect is especially striking in the carbon-reinforced composite where an appreciable residue (25 wt%) remains after exposure to 1130°C in air. The significance of this finding relative to ablation applications is not immediately evident. It may, however, be of considerable importance where high-temperature applications in air environment are contemplated.

With regard to phenyl substituted linear polyquinoxaline, the results of this work differ in several respects from the findings of an earlier study (Ref. 11). The earlier work reports an endotherm in the primary degradation regime and an exotherm in the 1300-1400°C regime, neither of which were observed in this study. Analytically, there are several other discrepancies. Cyanogen $(CN)_2$ could not be detected in the primary decomposition (565°C) process; the H_2 - HCN evolution process occurs at its maximum rate some 100°C higher than reported, and, finally, the evolution of N_2 in the 1000-1100°C regime (a major weight loss process) has not been previously reported, although there was evidence for it in the vapor phase chromatographic studies.

Several factors, some of which had been anticipated, impaired the quality of the isothermal degradation rate results. New equipment and techniques have been devised to overcome the detrimental effect of the exotherm by eliminating thermal excursions in the materials. Results which are now being generated may require a reevaluation of previously reported rate data.

An important contribution to an understanding of the degradation mechanisms should result from the development of an improved residue analysis. It is apparent from the mass spectral results that conventional analytical techniques are incapable of providing reliable results for nitrogen content of residues from heterocyclic nitrogen-containing polymers. This is the result of the extreme thermal stability of such residues under the conditions of these analyses. It appears that this is a general situation for nitrogen-containing heterocyclic polymers, since the result has been verified in this laboratory for a number of such polymers. The residue analyses reported here confirm the findings of the mass spectrometry experiments with respect to the principal mechanisms of degradation. Despite the limitations of these analyses the anticipated trends in hydrogen and nitrogen content as a function of temperature are substantiated.

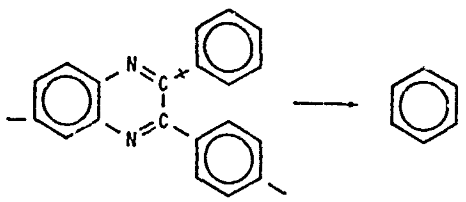
Mechanistically the critical step that leads to the formation of char is the primary decomposition process. The principal volatile products of the reaction are benzene, toluene, benzonitrile, and methane in order of decreasing importance. Crosslinked polyquinoxaline also evolves phenol, cresol, and carbon

monoxide as principal volatile products in this critical step. These products are directly attributable to the presence of phenylene oxide linkages. Subsequent steps merely remove small molecules from the three dimensional network formed in Step 1.

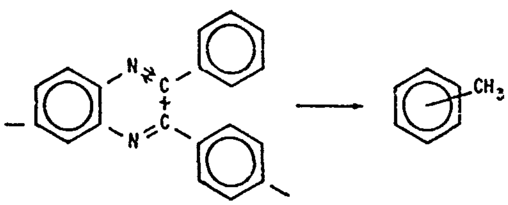
The detailed mechanisms of the degradation process remain incomplete and tentative, at best. Nevertheless, on the basis of results presented in this report the following generalizations are justified:

1. From a consideration of the structure of the basic unit in the polymer, the principal products appear to originate from rupture of the phenyl group from the quinoxaline ring and from rupture of the ring itself.

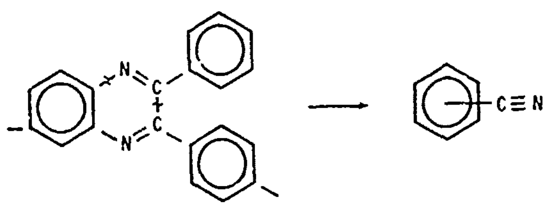
(1)



(2)



(3)



The above reactions competing simultaneously in decreasing order of importance may be summarized as follows:

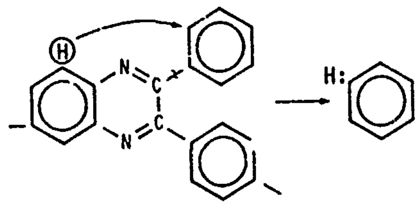
$$\text{(4) Polymer-I } (C_{34}H_{20}N_4) \xrightarrow{565^{\circ}C} C_6H_6 + C_6H_5CH_3 + C_6H_5CN + \text{Residue } (C_{26}H_{10}N_2)$$

This stated residue composition is consistent with the generalized reactions and also with the residue analysis obtained. An important reservation, however, is noted in the fact that the nitrogen analysis is assumed to be as much as 33% low. A more consistent residue composition, then, is $C_{26}H_{10}N_3$.

2. All of the principal products appear as complete molecules, hence, considerable hydrogen abstraction by the original fragments must occur before volatile species are released to the gas phase.

(5)

Typical:



3. The mass loss occurring in Step 1 can only account for the loss of approximately one phenyl and the degradation of one quinoxaline ring. The remainder becomes part of the intermediate solid product or prechar.

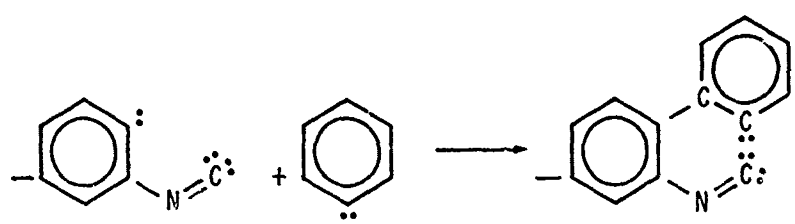
Hence, from a consideration of the above, it appears that the observed so-called primary products, with the possible exception of benzonitrile, are actually secondary products. That is, they are evidence of very reactive intermediates that escape from the quasi-solid state decomposition by stabilization resulting from hydrogen abstraction from neighboring aromatic groups. The remaining reactive species are either joined to the main mass and eventually couple to other reactive neighbors, or polymerize or recombine too rapidly to escape as volatile products.

Further support for this hypothesis comes from a consideration of the energetics of the reaction. Rupture of the quinoxaline ring should be an endothermic process, whereas an exotherm is observed. This indicates the occurence of an, as yet, unknown reaction or set of reactions, probably involving recombination, that are sufficiently exothermic to mask the endothermic processes.

The second step in the thermal degradation process is characterized by evolution of H_2 and HCN. Pendant nitriles in the intermediate residue are susceptible to cleavage. Cyclic nitrogen is assumed to be extremely stable because better than 50% of this element is retained up to 850°C. It is likely that the bulk of the cleaved quinoxaline rings are recyclized by recombination with reactive aromatic fragments.

(6)

Typical:



The final step in degradation and complete carbonization involves the very high temperature elimination of heterocyclic nitrogen in the molecular form. The elemental analyses provide some clues as to the compositions of the intermediate and final chars which are indicative of the transformations which occur in this step. The exact mechanisms involved, however, are not clearly understood. Nevertheless, an awareness of the existence of a nitrogen elimination process is necessary in order to anticipate the ablative performance of these materials. This final process requires large energy inputs and likely results from ring rupture of heterocyclic structures probably containing a single nitrogen atom per ring. In a real charring ablator situation, because of the temperature profile through the heat shield thickness, this process will occur simultaneously with that releasing benzene, toluene and benzonitrile. The latter vapors, percolating through the heated char will deposit carbon,

densifying the char and liberating hydrogen. The composition of the gases entering the boundary layer will consist of hydrogen and nitrogen. An important consequence of these processes in ablation will be their effect on the blowing term whose value depends on the molecular weight of the evolved gases. Ablation modeling will need to take into account these findings.

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APPENDIX

TEST DATA TABULATION

Table A-1. Mass Spectrometric Decomposition Product Analysis for Polymer I

Scan No. Temp. (°C) m/e	Empirical Formula	1 70	2 330	3 452	4a 510	4b 577	4c 590	5 640	6 700	7 750	(800	9 860	10 920
15	CH_3				3	145	158	104	67	38	4		
16	NH_2, CH_4				1,4	72,214	78,260	51,160	73,111	83,53	17,6	4,-	
17	OH, NH_3	18,-	11,3	13	9,3	10,139	14,100	2,82	9,132	5,123	8,30	6,2	9,-
18	H_2O	97	76	64	43	56	45	37	34	45	38	31	32
26	CN				4	22,34	30,25	41,7	67,-	54,-	22	10	6
27	HCN, C_2H_3			3,4	6,13	140,56	214,50	344,20	598,	390,-	167,-	97,-	48,-
28	CO.N_2	12,6	11,3	27,-	59,-	69,15	73,26	56,26	62,50	45,51	27,54	31,91	28.228
23	C_2H_4	-,4	-2			-,16	-,29	-,10	-6				
29		4		2	4	2	7	3					
Temp.					516	573	595	647					
37					7	32	29	3					
38					28	74	56	8					
39				4	100	298	160	23					
40					11	20	12	11					
41					13	24	12	10					
44	CO_2	6		15	12	8	10	10					
45					23	54	8	3					
46					23	36	11	1					
49				2	13	30	18	6					
50				4	114	390	195	40					
51	C_4H_3			10	119	423	204	24					
52	C_4H			7	105	353	172	17					
53				3	11	29	10	2					
Temp.					522	569	600	650					
61					7	33	12	4					
62				3	25	64	15	3					

Table A-1. Mass Spectrometric Decomposition Product Analysis for Polymer I (Continued)

Scan No. / m/e	Empirical Formula	1	2	3	4a	4b	4c	5	6	7	8	9	10
63				6	57	195	62	9					
64				4	14	44	17	3					
65				6	70	204	35	2					
66					17	38	13	4					
73					15	26	18	1					
74				4	48	140	56	9					
75				3	36	105	54	13					
76				9	111	409	190	48					
77				10	127	464	176	21					
78	C_6H_6			62	760	2445	1000	110					
79					96	164	53	8					
Temp.					527	565	607						
89				4	47	120	13	6					
90					28	66	16	2					
91				53	940	1906	135	10					
92	C_7H_8			48	812	1513	103	4					
93				6	67	176	40	7					
Temp.					533	557	610	657					
102						32	12	5					
103	C_7H_5N			18,26	455	1167	511	78					
104				6	44	105	48	11					
105				3	12	27	3	2					
106				7	26	64	5						
115					9	9	4						
116				2	10	35	14						
117					28	73	34						
152					22	22	18						
128							24	9					
Temp.				490	545	545	620	665					
130							15						

Table A-1. Mass Spectrometric Decomposition Product Analysis for Polymer I (Continued)

Scan No. / m/e	Empirical Formula	1	2	3	4a	4b	4c	5	6	7	8	9	10
153							18						
154							42						

Table A-2. High Temperature Magnetic Scans (m/e 12-28) for Polymer I

Temp. (^{o}C)	I_{CO}	I_{N_2}
955		450
973	45	520
990		598
1000		628
1007		710
1025	97	735
1035		701
1047		701
1060		726
1075		641
1090		624
1100	90	632
1113		516

Table A-3. Mas Spectral Decomposition Product Analysis (m/e 70+) for Polymer I

Scan No. Temp.(°C) m/e	Empirical Formula	1 240	2 345	3a 452	3b 516	3c 522	3d 578	3e 580	3f 645	4 653	5 700
73							50	51	6	4	
74					[illegible]	33	149	172	26	19	
75					16	20	158	136	25	22	
76				5	60	67	516	553	103	68	11
77				13	70	94	525	508	70	45	8
78	C_6H_6			36	320	393	2993	2864	381	241	35
79				3	27	43	223	200	30	19	
89				2	15	21	133	85	8		
90				2	10	14	77	63	5		
91				41	302	557	2232	1214	28	11	4
92	C_7H_8			30	223	425	1855	974	25	9	
93					18	53	204	148	20	6	
102						7	34	29	8	5	
103	C_7H_5N			16,16	129	265	1496	1278	390	149	24
104					13	26	127	114	39	14	
105					6	14	26	12	3		
106					13	18	28	47	4		
Temp.				475	510	532	573	587	638	660	705°C
115						2	14	14	5		
116						7	59	46	8		
117	C_8H_8N					16	113	108	15		
128							17	31	21	11	
130								20	13		
152						11	34	46	30	6	
153						8	35	46	19	2	
154	$C_{12}H_{10}$					23	106	167	67	15	
Temp.				494	500	540	563	595	630	668	

Table A-3. Mass Spectral Decomposition Product Analysis (m/e 70+) for Polymer I (Continued)

Scan No. / m/e	Empirical Formula	1	2	3a	3b	3c	3d	3e	3f	4	5
165						12	29	35	21	4	
166						8	20	26	19	7	
167						12	36	30	10	4	
168						20	42	47	13	3	
178								22	13	10	
179						5	7	34	12	22	
182							10	4			
Temp.						547	557	599	625	672	
206									12	11	

Table A-4. Mass Spectrometric Decomposition Product Analysis for Polymer II

Scan No. / Temp.(°C) / m/e	Empirical Formula	1 / 60	2 / 240	3 / 425	4a / 503	4b / 580	4c / 580	4d / 650	5 / 662	6 / 695	7 / 730	8 / 753	9 / 782	10 / 825	11 / 860
14									6,12	3,13					
15	CH_3				9	91	144	113	5,209	5,125	3,70	5,25	2,7	3	
16	NH_2				8	70	79	82	149	176	148	118	57	6	
16	CH_4				10	161	228	174	269	186	105	43	16	3	
17	OH	11	9	6	11	39	43	19	23	18	14	11	8	8	6
17	NH_3				10	113	136	153	274	283	260	154	73	24	10
18	H_2O	70	47	53	56	223	283	92	135	100	66	66	59	56	57
26	CN, C_2H_2				7,4	22,13	27,16	42,2	70,7	81,7	69,13	75,5	37,5	25,4	18,3
27	HCN				27	135	265	372	557	598	557	469	311	186	121
27	C_2H_3				10	42	37	6							
28	CO	22	25	23	40	418	756	497	520	460	427	311	190	82	77
28	N_2		6	6		12		52	139	242	348	269	218	154	200
28	C_2H_4		3	5	5	20	28	4	15	4	3		3	4	
Temp.					513	570	590	640	670	705	740	763	792	835	870
37						27	17								
38						56	47								
39					21	218	145	15							
40					10	98	36	10							
41					8	17	24	23							
44	CO_2	7	22	14	17	120	126	76	66	50	42	33	28		
45						10	[illegible]								
47					10	50	[illegible]								
50					14	126	31	28							
51	C_4H_3				21	155	114	24							
52	C_4H_4				16	55	66	11							
53						38,34									
55					16	88	26	6							

Table A-4. Mass Spectrometric Decomposition Product Analysis for Polymer II (Continued)

Scan No.	Empirical Formula	1	2	3	4a	4b	4c	4d	5	6	7	8	9	10	11
m/e															
61						20									
62					8	44	17								
63					17	104	34	8							
64						35	10	8							
65					34	263	78	8							
66					37	59	61	8							
Temp.					528	560	600°C	630							
74						31	23	5							
75						15	17	5							
76						56	73	46							
77					30	152	67	21							
78	C_6H_6				36	271	308	132							
79					15	10,57	28	13							
89						31									
90															
91	C_7H_7				102	367	123	30							
92	C_7H_8				67	246	88	18							
93					19	57	29	14							
94	C_6H_5OH				399	1379	166	42							
95					26	102									
103	C_7H_5N				22	97	158	114							
104					10	16		15							
106						44									
107					172	367	18	13							
108	C_7H_7OH				135	325	25	14							
109						28									
116						12	10								
117						20	19	15							
118							11								
119							11	12							
120					16	18									
122					25	28									
Temp.					538	540	610	620							
130					10			10							

Table A-5. Electrostatic S[illegible] of High Temperature Range (m/e 27-[illegible]) [illegible] Polymer II

Temp. (°C)	I_{HCN}	I_{CO}	I_{N_2}
895	102	97	500
922	70	103	802
940	55	103	952
960	50	102	1088
980	54	123	1170
992	50	129	1265
1007	44	129	1319
1032	43	135	1333
1050	39	146	1306
1075	35	149	1197
1090	33	176	1088
1105	32	200	1034

Table A-6. Mass Spectrometric Decomposition Product Analysis for Polymer III

Scan No. Temp (°C) m/e	Empirical Formula	1 415	2a 520	2b 597	2c 602	3 660	4 705	5 745	6 765	7 783	8 802
15	CH_3			70	86	97	76	45	23	15	4
16	NH_2,CH_4			49,149	30,144	42,149	44,107	62,53	61,50	24,16	10,-
17	$OH.NH_3$	3,2	9,3	12,56	7,60	8,67	7,85	3,94	5,73	6,53	3,17
18		38	31	45	47	41	35	23	29	24	28
26	CN,C_2H_2			16,20	31,16	50,12	82,-	70,-	76,-	56,-	29,-
27	HCN		4,6	119,27	149,38	376,-	598,-	598,-	581,-	390,-	250,-
28	CO	6	27	110	139	120	102	109	109	76	51
28	N_2	2	6	7	25	30	40	65	56	48	47
28	CH_2N,C_2H_4	-,2	-,2	-,15	-,24	-,9	-,7	-,6	-,4		
37				28	15						
38			[illegible]	67	53						
39			45	255	153	21					
40			7	32	6						
41			12	17	8						
45			21	37	9						
46			11	18							
49				42	20						
50			42	325	181	23					
51			67	390	181	31					
52	C_4H_4		48	316	190	22					
Temp.			528	585	615	670					
61			7	21	10						
62			16	51	15						
63			[illegible]	167	50						
64			9	40	15						
65			47	204	30						
66				70	19						

Table A-6. Mass Spectrometric Decomposition Product Analysis for Polymer III (Continued)

Scan No. / m/e	Empirical Formula	1	2a	2b	2c	3	4	5	6	7	8
73			6	43	23						
74			19	136	54						
75			17	82	47						
76			64	400	181	33					
77			76	460	176	26					
78	C_6H_6		38	2308	897	91					
79			25	149	57	11					
89			26	88	13						
90			12	59	12						
91	C_7H_7		557	1710	109						
92	C_7H_8		520	1282	104						
93			33	149	40						
94	C_6H_5OH		32	325	36						
Temp.			538	570	623	685					
103	C_7H_5N		232	1052	480	79					
104			16	94	37						
105				29							
106			14	58							
107				58							
108				58							
116				38	13						
117				88	33						
152				38	14						
153				35	21						
154	$C_{12}H_{10}$		21	103	53						
165			12	38	13						
166			6	23	14						
167			16	45	9						
168			21	61	14						
179				22							
Temp.			548	560	637						

Table A-7. Electrostatic Scan of High Temperature Range (m/e 27-28) for Polymer III

Temp. (°C)	I_{HCN}	I_{CO}	I_{N_2}
880	130	41	85
905	88	38	144
935	67	38	223
970	65	41	390
990	50	42	590
1010	50	46	620
1025	25	42	675
1045	30	41	727
1060	22	38	731
1077	20	38	727
1095	21	50	693
1110	16	45	641
1148	17	47	557
1230	17	70	297
1310		102	153
1392		158	111
1450		288	96

Table A-8. Mass Spectrometric Decomposition Product Analysis for Polymer IV

Scan No. / Temp. (°C) / m/e	Empirical Formula	1 / 25	2 / 250	3 / 435	4 / 490	5a / 545	5b / 627	6 / 650	7 / 710	8 / 750	9 / 775	10 / 815	11 / 833	12 / 858	13 / 895
15	CH_3					7	82	62	41	26	10	5			
16	O, NH_2, CH_4			2,2		1,6,20	1,22,107	31,100	-,38,63	-,27,54	-,14,17	-,7,3	-,3,2		
17	OH, NH_3	6	4	5,1		6,10	10,37	6,43	3,54	3,56	4,27	3,7	2,8	2	
18		14	17	13	14	42	41	30	20	18	12	12	15	15	n.s.
26	CN				3	12	11,8	27	75	95	56	37	22	14	5
27	HCN, C_2H_2				6	10,31	117,6	200,-	585,-	707,-	474,-	269,-	163,-	117	66
28	CO	4	5	14	29	85	111	132	127	123	70	45	38	30	28
28	N_2, CH_2N			3					43,10	67,-	53,-	43,-	36	33	46
28	C_2H_4			1		4	6	8	2	7		4	4		
37						19	5								
38						49	13								
39					28	214	41	20							
40						33									
41						16									
44	CO_2		6	17	11	10	8	13	15	12	7				
45					10	41									
46					5	25									
47					4	17									
49						17									
50				3	30	176	66	34							
51				4	37	195	75	28							
52				3	32	158	59	20							
53						23									
55						23									
Temp.				450	505	555	617	660	720	760	785				

n.s.: not scanned

Table A-8. Mass Spectrometric Decomposition Product Analysis for Polymer IV (Continued)

Scan No. / m/e	Empirical Formula	1 25	2 250	3 435	4 490	5a 545	5b 627	6 650	7 710	8 750	9 775	10 815	11 833	12 858	13 895
51						17	4								
62					7	42	10								
63					24	105	25	5							
64					8	24	8	4							
65				10	43	122	19	6							
66					14	56	13								
73						19	7								
74					9	62	28	9							
75					8	35	27	12							
76				4	26	138	91	45							
77				7	41	214	92	25							
78	C_6H_6			21	204	1061	558	108							
79					16	76	39	7							
89					26	49	16								
90					10	25	12								
91	C_7H_7			36	362	794	130	11							
92	C_7H_8			49	307	653	103	8							
93				10	26	62	29	8							
94	C_6H_5OH			10	94	381	67	1							
95					5	31	3								
Temp.				468	513	567	605	670							
103	C_6H_5CN				70	404	311	79							
104					12	39	30	7							
105					2	1	4								
106					7	2	10								
107					17	6	12								
108	C_7H_7OH				22	72	10								
116						25									
117	C_7H_7CN					31									
128							1	10							
130							8								

Table A-8. Mass Spectrometric Decomposition Product Analysis for Polymer IV (Continued)

Scan No. / m/e	Empirical Formula	1 25	2 250	3 435	4 490	5a 545	5b 627	6 650	7 710	8 750	9 775	10 815	11 833	12 858	13 895
152					5	20	19	1							
153					4	18	14	3							
154	$C_{12}H_{10}$				9	62	59	3							
155						11	12	4							
165					11	32	28	3							
166					6	28	24	4							
167					12	27	27	3							
168					16	39	20	3							
169						7	5								
170						12	7								
178								7							
179								8							
184						13									
Temp.					525	585	585	680							

Table A-9. Electrostatic Scan of High Temperature Range (m/e 27-28) for Polymer IV

Temp. (°C)	I_{HCN}	I_{CO}	I_{N_2}
925	66	32	85
943	55	30	135
967	50	28	186
995	40	30	250
1010	38	33	288
1028	37	38	334
1035	25	40	353
1043	24	40	381
1050	23	40	390
1058	20	41	381
1065	21	45	386
1083	18	47	367
1090	17	48	367
1098	20	53	344
1108	20	56	334
1117	20	59	325

Table A-10. Mass Spectrometric Decomposition Product Analysis for Composite Panel No. 6

Scan No.	1	2	3	4	5	6	7	8	9	10	11	12
Temp.	50	235	323	385	455	513	560	630	685	730	780	825
m/e												
15							23	60	35	33	10	
16							7,24	17,88	34,79	29,48	13,18	
17	10	6	10	6	7	4	11,16	10,33	6,55	6,50	9,23	3,7
18	60	37	37	30	41	34	44	44	41	[illegible]	37	27
26							10	22	63	73	56	21
27							32,22	148,21	409,30	626.-	423	204
28	13	17	39	21	28	51	105	126	123	146	88	50
28									24	56	43	37
28							7	8	6	3	8	
38							37					
39					10	70	122	20				
40							20					
44		21	43	25	19	20	14	17	15	14		
45						18	12					
46							12					
47							14					
49							20					
50					7	45	111	26	9			
51					8	60	152	28	6			
52					5	47	117	29	4			
Temp					467	525	577	645	703			
62						16	23					
63					5	52	52					
64						11	19					
65					11	88	75					
66						32	38					
73							19					
74						26	42	15				
75						17	40	12				
76					7	42	98	37	7			
77					11	67	126	29	11			
78					33	325	661	135	23			
79					4	30	51	12	3			

Table A-10. Mass Spectrometric Decomposition Product Analysis for Composite Panel No. 6 (Continued)

Scan No. / Temp, °C / m/e	1	2	3	4	5	6	7	8	9	10	11	12
					467	525	577	645	703			
89						27	20					
90						20	14					
91					65	457	269	11				
92					50	415	204	10				
93					6	35	39					
94					26	223	158					
95						23	13					
Temp					485	535	588	650	710			
103					2	117	255	100	13			
104						13	30	10				
106						11	10					
107						31	22					
108						33	24					
116							18					
117							16					
154						30	50					
165						13	20					
166						12	18					
167						16	11					
168						21	17					
169						6						
170						14						
Temp.						550	605					

Table A-11. Mass Spectrometric Decomposition Product Analysis (m/e 70-108) for Composite Panel No. 6

Temp. °C	78	91	94	103	107	108
350	3	7	3			
	3	10	5			
	3	9	8			
	3	5	6			
	3	5	9			
	3	4	7			
	3	3	3			
	3	6	6			
452	3	9	11	3		
472	3	35	22	7		
495	3	54	35	8		
507	90	108	53	29	8	
515		153	97	44	10	
527	176	223	130	54	13	
537		269	158	83	17	31
552	302	232	200	111	20	24
563		265	177	139	22	27
573	325	210	146	171	26	23
580		172	114	167	17	18
595	251	120	68	167	14	11
601	278	65	42	139	4	6
615	172	43	26	121	3	2
627	141	23	15	93		
640	74	14	6	81		
652	74	9	3	45		
672	38			38		
708	17			12		
736	5			5		

Table A-12. Electrostatic Scan of High Temperature Range (m/e 27-28) for Composite Panel No. 6

TEMP.	I_{HCN}	I_{CO}	I_{N_2}
860	176	59	38
897	108	53	42
943	70	48	88
970	64	43	117
995	61	46	176
1010	55	40	204
1025	50	44	251
1043	50	48	278
1060	39	52	306
1075	35	60	316
1090	28	62	304
1107	26	65	283
1115	25	68	274
1123	24	72	260